4-*n*-Amyl-2-*n*-valerylphenol.—A mixture of 82 g. (0.5 mole) of 4-*n*-amylphenol and 76 g. (0.75 mole) of *n*-valeric acid was cooled at 25–30° while 54 g. (0.79 mole) of boron trifluoride was absorbed during about 0.5 hour. The mixture stood for 15 min., then was heated by an electric mantle to 140° during 12 min., and was held at 140–150° for one hour.

The red-amber solution was poured into 250 g. of sodium acetate in 600 ml. of water. The organic layer was washed with 500 ml. of 5% sodium carbonate and 500 ml. of water and concentrated. Distillation gave 95 g. (77%), b.p. 122–127° (0.5 mm.).

2,4-Di-*n*-amylphenol.—A small shaking autoclave was charged with 124 g. (0.5 mole) of 4-*n*-amyl-2-*n*-valerylphenol, 10 g. of copper chromite catalyst and hydrogen at 130 atm. Reduction started at 155° and 170 atm. and was complete in 0.5 hour, the temperature rising to 182° during the reaction. The reaction mixture was diluted with about 600 ml. of methanol and the catalyst was filtered off. The filtrate was concentrated, diluted with benzene and heated to codistil water. Distillation gave 96.5 g. (82%), b.p. 110° (0.5 mm.).

2,4-Di-*n*-amylphenyl N-(1-naphthyl)-carbamate.—A mixture of 2.34 g. (0.01 mole) of 2,4-di-*n*-amylphenol, 2.03 g. (0.012 mole) of α-naphthyl isocyanate and three drops of pyridine was heated on a steam-bath for 2 hr. Addition of 20 ml. of petroleum ether and stirring gave a solution from which 3.73 g. (93%) of the urethan, m.p. 101–102.5°, separated. Recrystallization from ethanol raises the melting point to 104–104.5°. *Anal.* Calcd. for $C_{27}H_{33}NO_2$: C, 80.4; H, 8.2; N, 3.5. Found: C, 80.2; H, 8.0; N, 3.8.

Allyl 4-*n*-Decylphenyl Ether.—A mixture of 23.4 g. (0.1 mole) of 4-*n*-decylphenol, 14.5 g. (0.12 mole) of allyl bromide, 20 g. of freshly ignited anhydrous potassium bromide and 200 ml. of anhydrous acetone was stirred under reflux for 7 hr. Dilution with an equal volume of water gave an oil which was extracted into petroleum ether (three 100-ml. portions). The extract was washed with 100 ml. of 2.5% sodium hydroxide; the emulsion was broken by adding a little methanol and more water. After several washings with alkali, then with water, the petroleum ether solution was dried over magnesium sulfate, filtered and concentrated, giving 25 g. of colorless oil. Vacuum fractionation gave 23.2 g. (85%) of product, b.p. 132–136° (1 mm.), n^{25}_D 1.4937. *Anal.* Calcd. for $C_{19}H_{30}O$: C, 83.2; H, 11.0. Found: C, 83.6; H, 10.6.

2-Allyl-4-*n*-decylphenol.—A small flask containing 22.5 g. (0.082 mole) of allyl 4-*n*-decylphenyl ether was heated in an oil-bath to 235° during one hour. An exothermic reaction raised the melt temperature to 244.5° while the bath remained at 238°. The bath was held at 238° for 15 min. longer and was then removed. Distillation of the melt gave 19.8 g., b.p. 140–150° (1 mm.). Refractionation yielded 17.2 g. (76%), b.p. 143–148° (1 mm.), n^{25}_D 1.5034. An amorphous white solid present in the distillation column may be evidence of polymerization.

4-*n*-Decyl-2-*n*-propylphenol.—A mixture of 17.1 g. (0.062 mole) of 2-allyl-4-decylphenol, 85 ml. of absolute ethanol and a small amount of Raney nickel catalyst was shaken under hydrogen at 2.7 atm. Reduction was complete in a few minutes. The catalyst was filtered off and the filtrate concentrated to an oil. The latter was fractionated twice, giving 13.9 g. (81%), b.p. 146–150° (1 mm.), n^{25}_D 1.4960.

The α-naphthylurethan prepared as just described melted at 87–88° after two crystallizations from *n*-heptane and one from ethanol. A mixed melting point with the urethan obtained from 4-*n*-decyl-2-*n*-propylphenol prepared *via* the propionyl compound was not depressed.

4-*n*-Amyl-2-(1-methyl)-butylphenol.—To 0.3 mole of methylmagnesium iodide in 120 ml. of ethyl ether was added 23.4 g. (0.1 mole) of 4-*n*-amyl-2-butyrylphenol in 120 ml. of ethyl ether during 20 min. The clear, gray-green solution was refluxed for 3 hr. longer, then poured into 500 ml. of ice. Following the addition of 70 ml. of 5 *N* sulfuric acid, the organic layer was separated and the aqueous layer extracted with two 100-ml. portions of ethyl ether. The ether solution was washed with water, dried over magnesium sulfate, and concentrated. The oil was dissolved in 200 ml. of benzene and the solution, following addition of 5 g. of anhydrous oxalic acid, refluxed under a Dean–Stark trap for 3 hr. The reaction mixture was washed with 100 ml. of water, 100 ml. of 5% sodium carbonate and four 100-ml. portions of water. Following concentration, the residue was vacuum distilled, giving 22.2 g. (95%) of 4-*n*-amyl-2-(1-methyl-1-butenyl)-phenol, b.p. 95–109° (1 mm.) mostly at 106–109°. The material was not purified further but immediately hydrogenated at 2.7 atm. in the presence of Raney nickel and ethanol. The filtrate was concentrated to an oil which was dissolved in 200 ml. of benzene and washed with 100 ml. of 5% hydrochloric acid and five 100-ml. portions of water. Fractional distillation gave 20.3 g. (91%) of product, b.p. 157–159° (7 mm.), n^{25}_D 1.5019. Equally good material was prepared *via* 4-*n*-amyl-2-*n*-butyrylanisole, b.p. 171–174° (6 mm.), n^{25}_D 1.5096. *Anal.* Calcd. for $C_{16}H_{24}O_2$: C, 77.4; H, 9.7. Found: C, 77.8; H, 9.6, prepared by methylation of 4-*n*-amyl-2-*n*-butyrylphenol, and 4-*n*-amyl-2-(1-methylbutyl)-anisole, b.p. 147–151° (6 mm.), n^{25}_D 1.4930. *Anal.* Calcd. for $C_{17}H_{28}O$: C, 82.2; H, 11.3. Found: C, 82.5; H, 11.2.

2,4-Di-*sec*-butylphenol and 2,4,6-tri-*sec*-butylphenol were prepared *via* the reaction of the keto-phenols with excess Grignard reagent, as just described, followed by hydrogenation.

ROCHESTER 4, N. Y.

[CONTRIBUTION FROM THE SHELL DEVELOPMENT CO.]

The Use of Cupric and Ferric Chlorides in the Trapping of Radical Intermediates and the Synthesis of Alkyl Chlorides

BY J. KUMAMOTO, H. E. DE LA MARE AND F. F. RUST

RECEIVED JUNE 2, 1959

Alkyl radicals derived from di-*t*-butyl peroxide, *t*-butyl hydroperoxide, 2-tetrahydropyranyl hydroperoxide, 2,5-dimethyl-2,5-dihydroperoxyhexane and azo-bis-isobutyronitrile have been trapped by the use of metal halides such as ferric and cupric chlorides. In the trapping process, an alkyl radical is converted to the corresponding alkyl chloride. A mechanism involving one electron transfer through a chloride bridge is proposed.

Introduction

An area of considerable interest in free radical chemistry concerns the nature of primary and intermediate radical species. Since end products do not always conclusively establish the identity of an intermediate radical, much attention has been given to the chemical interception of such intermediates. The present work is concerned primarily with the capture of alkyl radicals in solution by the general process

$$R\cdot + \text{metal}^{n}(\text{chloride})_{n} \longrightarrow RCl + \text{metal}^{n-1}(\text{chloride})_{n-1}$$

This technique has recently been used for intercepting growing polymer chains,[1] and reported and interpreted for its use in homolytic addition to

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(1) C. H. Bamford, A. D. Jenkins and R. Johnston, *Proc. Roy. Soc.* (*London*), **A239**, 214 (1957).

olefins.[2] The production of alkyl chloride in the reaction of oxaziranes with ferrous chloride is undoubtedly an example of the same general phenomenon.[3]

Results

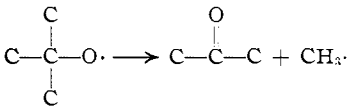
Azo-bis-isobutyronitrile (AIBN).—The reactivity of various cupric salts with isobutyronitrile radicals (from the liquid phase thermal decomposition of azo-bis-isobutyronitrile) was qualitatively assessed by visually observing the rate at which the blue color of cupric ion disappeared. Cupric chloride and bromide in dioxane–water were found to be reactive, while cupric acetate gave a qualitatively negative test. Cupric acetate in propionic acid gave a doubtful result.

The decomposition of AIBN in absolute ethanol containing ferric chloride did not give a visible color change but precipitation with hydroxide indicated some reaction of the ferric salt had taken place.

The rate of decomposition of AIBN was measured by following its reaction with cupric chloride. Although there was no attempt to maintain a constant ionic strength, the effect of variations of concentration of 10:2:1 in AIBN and 2.5:1 in cupric ion on the initial slope showed a first order dependence on AIBN and zero order dependence on cupric ion. The half-life value found was 3.4 ± 0.3 hr. at 75° which agreed with the previously reported value 3.3 hours.[4]

Product isolation work on the reaction of AIBN with cupric chloride in dioxane–water resulted in the isolation of 2-chloro-2-methylpropionitrile. Although extensive product work was not done, chlorine analysis of a dioxane forerun and concentrate indicated that a maximum of ~55% of the AIBN radicals could be accounted for as the chloronitrile (see Experimental).

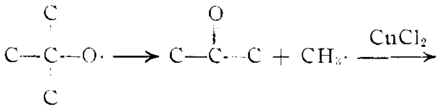
***t*-Butyl Hydroperoxide.**—The ferrous ion decomposition of *t*-butyl hydroperoxide has been shown to give *t*-butoxy radicals[5] which subsequently cleave to yield methyl radicals[6]



$$\text{C}-\underset{\text{C}}{\overset{\text{C}}{\text{C}}}-\text{O}\cdot \longrightarrow \text{C}-\overset{\text{O}}{\text{C}}-\text{C} + \text{CH}_3\cdot \quad (1)$$

The principal gaseous products with ferrous sulfate and ferrous ammonium sulfate are methane and ethane. When either ferrous chloride or cupric chloride is used, the predominant gas is methyl chloride with small amounts of methane and ethane (see Experimental).

The reaction of pure *t*-butyl hydroperoxide with an aqueous solution of ferrous sulfate–cupric chloride has been examined in some detail and a product balance is shown in Table I. The data suggest that part of the acetone is produced during workup since the summation of non-condensable C_1 compounds is < 50% of the total acetone found. Alternatively, part or all of this discrepancy may be due to the production of some C_1 non-gaseous materials, *e.g.*, methanol or methyl sulfate, or incomplete recovery of methyl chloride. Methanol was not detected by g.l.c. (gas liquid chromatography), but no attempt was made to identify or determine methyl sulfate. However, it is clear that methyl radical capture by cupric chloride is a very efficient process



$$\text{C}-\underset{\text{C}}{\overset{\text{C}}{\text{C}}}-\text{O}\cdot \longrightarrow \text{C}-\overset{\text{O}}{\text{C}}-\text{C} + \text{CH}_3\cdot \xrightarrow{\text{CuCl}_2} \text{CH}_3\text{Cl} + \text{CuCl} \quad (2)$$

The greater alkoxy cleavage where metal ion is added to peroxide (b, Table I) probably reflects less capture of RO· radicals by electron exchange with ferrous iron ($\text{RO}\cdot + \text{Fe}^{++} \xrightarrow{\text{H}_2\text{O}} \text{ROH} + \text{FeOH}^{++}$). This latter process would be expected to be more important where peroxide is added to excess ferrous sulfate (*a*, Table I).

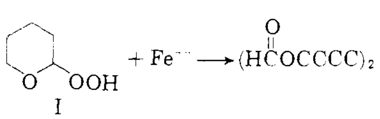
Table I

Products from the Reaction of *t*-Butyl Hydroperoxide with Ferrous Sulfate–Cupric Chloride at 0–5°

Product	Moles/100 moles of peroxide reacted (a)[a]	(b)[b]
t-Butyl alcohol[c]	82	63
Acetone	18	37
Methyl chloride	~6.9	16
Methane	<0.9	<0.04
Ethane		0.24

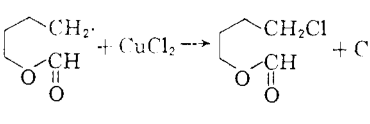
[a] The peroxide was added to the ferrous sulfate–cupric chloride. [b] Ferrous sulfate was added to the peroxide–cupric chloride solution. [c] Determined by the difference: reacted hydroperoxide–acetone. g.l.c. showed that acetone and *t*-butyl alcohol were the only products, although trace quantities may not have been detected.

2-Tetrahydropyranyl Hydroperoxide (I).—A ferrous chloride solution was dripped into a solution of I and cupric chloride in water. A 36% yield of 4-chloro-1-butylformate was isolated. The decomposition in the absence of halide (ferrous sulfate) produces the dimer.[7]



I (3)

In the presence of cupric chloride or ferric chloride, the dimerization is replaced principally by[8]



(4)

2,5-Dimethyl-2,5-dihydroperoxyhexane (II).—When one treats 2,5-dimethyl-2,5-dihydroperoxyhexane with ferrous sulfate one obtains along with other compounds[9] a substantial gas production

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[2] J. K. Kochi, This Journal, **78**, 4815 (1957).

[3] W. D. Emmons, *ibid.*, **79**, 5745 (1958).

[4] C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, *ibid.*, **71**, 2661 (1949).

[5] M. S. Kharasch, F. J. Arimoto and W. Nudenberg, *J. Org. Chem.*, **16**, 1556 (1951).

[6] J. H. Raley, F. F. Rust and W. E. Vaughan, This Journal, **70**, 88 (1948).

[7] E. A. Youngman, G. M. Coppinger and H. E. De La Mare, unpublished work from this Laboratory.

[8] The reaction leading to organobromide may be effected using the metallic bromides.

[9] See Experimental.

(ethylene, ethane and butane in amounts dependent on the environment). However, in a given medium (*e.g.*, *t*-butyl alcohol–water) the relative amounts of these gases appear to be roughly the same irrespective of the manner of addition (peroxide to iron or *vice versa*) (see Table II).

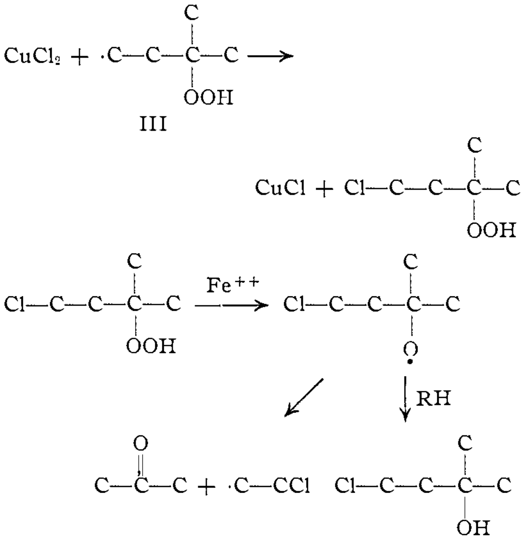
TABLE II

REACTION OF FERROUS SULFATE WITH 2,5-DIMETHYL-2,5-DIHYDROPEROXYHEXANE. GASEOUS PRODUCTS AT 25–40°

Product	Moles/100 moles of peroxide (a)[a]	 (b)[b]
Ethylene	21.0	18.6
Ethane	3.0	3.2
Butane	5.8	3.8

[a] Peroxide (*t*-butyl alcohol solution) added to excess ferous sulfate. [b] An equivalent amount of ferrous sulfate was added to the peroxide (*t*-butyl alcohol solution).

When the decomposition of this dihydroperoxide (0.20 mole) is effected in the presence of cupric chloride, gas production is quenched and 4-chloro-2-methyl-2-butanol ($\leqq$0.064 mole) as well as 1,2-dichloroethane ($\sim$0.01 mole) appear among the products. These products are believed to arise by the sequence shown in (5) to (8)



(5)

(6)

(7)

$$\text{Cl—C—C}\cdot + \text{CuCl}_2 \longrightarrow \text{Cl—C—C—Cl} + \text{CuCl} \quad (8)$$

Thus, an important intermediate radical (III) is tagged by reaction with cupric chloride.

Di-*t*-butyl Peroxide (DTBP).—Vapor phase thermal decomposition of DTBP[10] in a vessel whose walls were coated with curpic chloride, at 122° and 132°, resulted in significant yields of methyl chloride. As the cupric chloride was consumed by subsequent runs, the methyl chloride yield decreased while the hydrocarbon yield increased.

TABLE III

ANALYSIS OF THE PRODUCTS FROM THE DECOMPOSITION OF DTBP OVER CUPRIC CHLORIDE AT 132°

Product	Moles/100 moles of DTBP Run 1	 Run 2
CH_3Cl	11.4	6.7
C_2H_6	6.3	23.1
CH_4	10.3	25.0
$(CH_3)_3CCl$	$\sim$150.0	

The *t*-butyl chloride presumably arises from a non-radical process.

Discussion and Conclusions

Taube[11] has demonstrated conclusively that some inorganic one electron oxidation–reduction reactions proceed by a mechanism involving the transfer of an anion, *e.g.*, chloride. Furthermore, the transfer of the anion occurs from the oxidizing agent to the reducing agent.

The examples presented in this current work are best rationalized in terms of such a chlorine-bridged transition state in which chlorine is transferred to an alkyl radical by an oxidizing metal ion

$$R\cdot + M^nCl_n \longrightarrow [R\cdots Cl\cdots M^nCl_{n-1}] \longrightarrow RCl + M^{n-1}Cl_{n-1} \quad (9)$$

Two kinetically indistinguishable paths for the formation of methyl chloride appear worthy of consideration:

$$\text{(A)}\quad CH_3\cdot + CuCl_2 \longrightarrow RCl + CuCl \quad (10)$$

with the oxidation reduction proceeding *via* a "chlorine bridge" or

$$\text{(B)}\quad (CH_3)_3C\text{—}O\cdot + CuCl_2 \longrightarrow CH_3Cl + CH_3COCH_3 + CuCl \quad (11)$$

involving direct metal to oxygen interaction or intermediate hypochlorite formation

The absence of methanol suggests that a process leading to a carbonium ion is unlikely, *viz.*

$$CH_3\cdot + CuCl_2 \longrightarrow CH_3^+ + CuCl + Cl^- \quad (12)$$

$$CH_3^+ \xrightarrow{H_2O} CH_3OH$$

Similarly, there is no evidence for intermediate hypochlorite formation (B), although this path cannot be rigorously excluded. Therefore, process (A) appears to be the more plausible path. The data from the AIBN work, showing the disappearance of cupric ion to be zero order in Cu^{++}, likewise favor a mechanism of type A, *i.e.*, cupric ion is not attacking AIBN directly.

The successful capture of the intermediate alkyl radicals from 2-tetrahydropyranyl hydroperoxide and 2,5-dimethyl-2,5-dihydroperoxyhexane are in agreement with process A, and require no additional explanation to be rationalized on this basis.

It will be noted that the reactions described here use stoichiometric amounts of cupric or ferric chloride. Reactions recently reported by Kharasch and Fono[12] use catalytic amounts of cuprous chloride and therefore are not productive of alkyl chlorides as major products.

The synthetic utility of these reactions should not be overlooked. In many cases where the cyclic organic hydroperoxide is readily available, it affords a convenient one-step synthesis to a bifunctional derivative (chloroacid,[13] chloroester, chloroketone, etc.).

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[10] J. H. Raley, F. F. Rust and W. E. Vaughan, ref. 6.

[11] H. Taube and H. Meyers, THIS JOURNAL, **76**, 2103 (1954).

[12] M. S. Kharasch and Andrew Fono, *J. Org. Chem.*, **23**, 324 (1958).

[13] The reaction of the cyclohexanone–hydrogen peroxide adduct with ferrous chloride, *e.g.*, has been shown (unpublished work from this Laboratory) to give good yields of 6-chlorohexanoic acid. Detailed work in this system will be reported later.

Experimental

Materials. t-Butyl Hydroperoxide.—The commercial Lucidol product was steam distilled to leave a crude hydroperoxide (~80%) which was further purified by vacuum fractionation. The material used for the experiments of Table II analyzed 99.7% by iodometric analysis and had a f.p. of 5.4°. Material used for the work of Table IV was of 85 to 90% purity by iodometric analysis.

2,5-Dimethyl-2,5-dihydroperoxyhexane.—This solid hydroperoxide was made by air oxidation of the hydrocarbon (oxygen/atm. press.),[14] or by reaction of the diol with hydrogen peroxide and sulfuric acid. The solid was purified by dissolution in ether and reprecipitating with Skelly B or by slurrying in Skelly B containing ~5% ether–5% ethanol; m.p. 104–105°, 96.5%w. by iodometric analysis.

2-Tetrahydropyranyl Hydroperoxide.—Hydrogen peroxide was added to dihydropyran to produce the desired hydroperoxide.[15]

Di-*t*-butyl Peroxide.—Shell Chemical product was used as such.

Azo-bis-isobutyronitrile.—Product of Monomer-Polymer Corp. was recrystallized from ether.

All inorganic chemicals used were reagent grade materials, usually the available hydrated salt.

Product Workup and Identification. Di-t-butyl Peroxide.—The system used was identical to that described earlier.[6] The reaction flask was coated with cupric chloride. Five grams of cupric chloride was dissolved in 10 ml. of water. The water was evaporated by warming the flask under vacuum with a burner while rotating to distribute the salt evenly. One gram of DTBP was allowed to react for three days at 122° or 132°.

The principal product, ~75%, was *t*-butyl chloride. Analysis of the gases was carried out by mass spectrometric methods. The *t*-butyl chloride was analyzed by g.l.c.

Azo-bis-isobutyronitrile.—AIBN, roughly 0.5 g., was added to 5 ml. of dilute dioxane–water solution of cupric salt in a glass tube and sealed off. The tube was heated in boiling water for *ca.* 9 minutes for qualitative observation. A control with all the ingredients except AIBN was carried out in each case.

The disappearance of cupric ion was followed at 700 mμ using a Cary spectrophotometer cell which was thermostated at 75°. The rates were determined from initial slope approximation taken after an induction period. With cupric at 0.1 *m*, AIBN was varied: 0.1 *m*, 0.05 *m*, 0.01 *m*. With AIBN at 0.1 *m*, cupric was used at 0.1 and 0.04 *n*. The solvent was dioxane–water, 50:50 by volume.

In the product isolation run, the reaction was carried out by treating 19 g. (0.116 mole) of AIBN with 40 g. (0.235 mole) of cupric chloride dihydrate in dioxane–water (~300 ml.:150 ml.). After refluxing for ~20 min. and allowing to stand for several months at room temperature, 10.4 g. of inorganic solid (cuprous + cupric salts) was filtered off. The filtrate was diluted with water and extracted several times with ether. After distillation of the bulk of the ether, a dioxane forerun (b.p. ~77–102°, n^{22}D 1.4159–1.4191, 63.1 g., 2.95% Cl) was collected; g.l.c. of the dioxane–concentrate (19.3 g., 11.8% Cl) remaining indicated a rough composition of 60% dioxane and 40% compound X; g.l.c. analysis also showed the chlorine-containing component of the forerun to be the same as X. Assuming all the Cl to be present as 2-chloro-2-methylpropionitrile, a maximum yield of 0.123 mole of the chloronitrile was produced.

A 17-g. aliquot of the dioxane concentrate was dissolved in petroleum ether and thoroughly water-washed. At this point, 0.6 g. of a crystalline product (m.p. 162–165°) whose infrared spectrum was compatible with tetramethylsuccinonitrile was filtered off. The petroleum ether extract was distilled and 2.6 g. of crude 2-chloro-2-methylpropionitrile (b.p. ~110°,[16]) n^{20}D 1.4012 to 1.4041) was collected; g.l.c. analysis of the fraction having n^{20}D 1.4041 (lit. values:[17]) b.p. 114–115°, n^{25}D 1.4045–1.4049) indicated it to be the same as compound X, but showed that it still contained a small amount of dioxane (see analyses). *Anal.* Calcd. for C_4H_6ClN: C, 46.4; H, 5.85; Cl, 34.3; N, 13.5; Found: C, 46.8; H, 6.3; Cl, 33.4; N, 12.6. The infrared spectrum was identical with the authentic spectrum of **2-chloro-2-methylpropionitrile** corrected for dioxane impurity.

The residue (2.1 g.) from the distillation of the petroleum ether extract was slurried in petroleum ether and 1.0 g. of crystalline material filtered off (m.p. 61–84°). This latter material was fractionally crystallized to give some unreacted AIBN and at least one other unidentified component (m.p. 59–61°, $C_{8.0}H_{13}N_{2.0}O_{1.6}$).

t-Butyl Hydroperoxide.—The decomposition of *t*-butyl hydroperoxide was carried out under nitrogen by dripping the ferrous salt into 10 ml. of hydroperoxide dissolved in 100 ml. of water. Reagents were cooled but the reaction was carried out at ambient temperature. The gaseous products were collected over water in a Podbielniak bottle and a sample taken for mass spectrometric analysis. The results obtained are listed in Table IV. The methyl chloride produced in the first three examples can be presumed to arise from the reaction of ferric ion which is formed during the decomposition of the hydroperoxide.

TABLE IV

GASEOUS PRODUCTS FROM THE DECOMPOSITION OF *t*-BUTYL HYDROPEROXIDE

Amount of metal salt	Moles/100 moles of hydroperoxide (mass spec. analysis) CH_3Cl	C_2H_6	CH_4
20 g. $FeCl_2$ in 60 ml. H_2O	21.8	0.8	2.0
20 g. $FeCl_2$ + 5 g. LiCl in 60 ml. H_2O	16.6	0.7	1.8
20 g. $FeCl_2$ + 10 g. NH_4Cl in 70 ml. H_2O	22.5	0.8	2.1
39 g. $Fe(NH_4)_2(SO_4)_2$ in 70 ml. H_2O	..	8.0	9.2
27 g. $FeSO_4$ in 70 ml. H_2O	..	2.2	2.7
20 g. $FeCl_2$ in 70 ml. H_2O (20 g. $CuCl_2$ added to peroxide phase)	30.2	<0.1	<0.1

The experiments reported in Table I were done in a closed-system, the gases being collected over brine in a three-necked Podbielniak bottle. The contents of the reaction vessel were magnetically stirred and the system flushed with nitrogen prior to the reaction. To ensure equilibration of the gases throughout the system, a small gas-circulating pump was inserted in the system. Gas samples were taken at the Podbielniak bottle after equilibration and analyzed by mass spectroscopy.

The additions of the peroxide to the aqueous ferrous sulfate–copper chloride solution or the ferrous sulfate to the copper chloride–peroxide solution were carried out at ~0.5°. The reaction mixtures were allowed to stand overnight and then stirred for 2 to 3 hours at room temperature. The products were rapidly distilled *in vacuo* (kettle temp. <40°) and the distillate was analyzed qualitatively by g.l.c. methods, and quantitatively for carbonyl and unreacted hydroperoxide by functional group methods.

2-Tetrahydropyranyl Hydroperoxide.—Ferrous chloride (20 g., 0.1 mole, in 70 ml. of water) was dripped into 0.1 mole of hydroperoxide in 100 ml. of water which contained 20 g. of cupric chloride, 0.12 mole (ferric chloride was also used in place of cupric chloride with the same results). Two runs were combined, extracted three times with ether, and dried over magnesium sulfate. The product was vacuum distilled, 76–79° (15 mm.), n^{20}D 1.4363. A 10-g. (36%) yield of 4-chloro-1-butyl formate was isolated. *Anal.* Calcd. for $C_5H_9O_2Cl$: C, 44.0; H, 6.6; Cl, 26.0; ester value, 0.73 equiv./100 g. Found: C, 44.4; H, 6.9; Cl, 26.1; formate value, 0.71 equiv./100 g.; ester value 0.693 equiv./100 g.

2,5-Dimethyl-2,5-dihydroperoxyhexane (in the Absence of Cupric Chloride).—Ferrous sulfate (0.214 mole) was added to an aqueous slurry of 2,5-dimethyl-2,5-dihydroperoxyhexane (0.102 mole, 97%w.) in a system similar to that described for *t*-butyl hydroperoxide. The addition was controlled to keep the temperature in the range 25 to 40°. Gases (0.0315 mole, principally ethane, butane and ethylene) were analyzed by mass spectrometry, and the volatile products were isolated by steam distillation and analyzed by g.l.c. and functional group methods. Acetone was by far the principal product (~0.16 mole). In addition, *t*-amyl alcohol, 2-methyl-2-hexanol, ethanol and methanol[18] were identified by correlation of emergence time with authentic samples. Ethyl *t*-amyl peroxide was isolated by trapping

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(14) See also F. F. Rust, THIS JOURNAL, **79**, 4000 (1957).

(15) N. A. Milas, *ibid.*, **76**, 2322 (1954).

(16) Micro distillation assembly did not permit accurate determination of b.p., probably low.

(17) C. L. Stevens, THIS JOURNAL, **70**, 166 (1948).

(18) Total hydroxyl value ≈0.01 mole.

from a large capacity g.l.c. column; $n^{20}\text{D}$ 1.3978. It was identified by its infrared and mass spectra, the latter indicating a molecular weight of 132. *Anal.* Calcd. for $C_7H_{16}O_2$: C, 63.6; H, 12.2. Found: C, 64.8; H, 12.3. The principal impurity was an unidentified carbonyl as shown by infrared analysis.

RELATIVE AREAS (~% W.) AS DETERMINED BY G.L.C. (UNCALIBRATED)-ANALYSIS ON DIISODECYL PHTHALATE PACKING

Product	Weight. %
Methanol	0.8
Acetone	76.6 (prob. includes some ethanol ≤3%)
Methyl ethyl ketone	~0.8
t-Amyl alcohol	3.2
Ethyl *t*-amyl peroxide	16.1
2-Methyl-2-hexanol	2.4

2,5-Dimethyl-2,5-dihydroperoxyhexane (in the Presence of Cupric Chloride).—Cupric chloride (1.0 mole in 100 ml. of H_2O + 150 ml. of CH_3OH) was mixed with the methanolic solution of the peroxide (0.2 mole/250 ml. of methanol), and ferrous sulfate (0.48 mole/250 ml. of water) was added to maintain a temperature of 25–40°. Gas production was nil. The crude reaction mixture was distilled (I) through a 20-cm. heli-grid column until ~438 g. of distillate were collected. This distillate was refractionated (after removal of a 20-g. aliquot for analyses) in a 100-cm. helice-packed column (distillation II). Fractions 1 to 4 (95.2 g., b.p. 55.5–64.5°, $n^{20}\text{D}$ 1.3345 to 1.3290) were analyzed by mass spectrometry: 1.6% mole 1,2-dichloroethane, 6.8% mole acetone and 92% mole methanol; g.l.c. analyses were qualitatively consistent with this analysis. On the basis of a chlorine analysis (0.52 %), the amount of 1,2-dichloroethane was calculated to be 0.0074 mole. Methanol is known to azeotrope with the 1,2-dichloroethane (b.p. 60.95°).[19]

The concentrate remaining from distillation II was saturated with potassium carbonate and extracted with ether. The ether extract was combined with the extract obtained by continuous extraction of the original aqueous inorganic salt phase.[20] The ether was distilled and the residual liquid was fractionated (distillation III) to give four volatile fractions (3 to 6) containing chlorine and hydroxyl groups.

An authentic sample of 4-chloro-2-methyl-2-butanol (β-chloro-*t*-amyl alcohol; b.p. 53–54° (6 to 7 mm.), $n^{20}\text{D}$ 1.4446; lit. value[21] b.p. 62–63° (14 mm.)) was prepared from ethyl β-chloroacetate and methylmagnesium iodide, and its infrared spectrum recorded. *Anal.* Calcd. for $C_5H_{11}OCl$: C, 49.0; H, 9.05; Cl, 28.92. Found: C, 49.3; H, 9.1; Cl, 28.6.

Direct comparison of the authentic spectrum of β-chloro-*t*-amyl alcohol with fractions 3 to 6 and g.l.c. analyses established the presence of that alcohol as a principal constituent of each fraction. Chlorine analyses (21.6%) of a sample simulating the composition of fractions 4 to 6 placed on upper limit of 74.5% (0.05 mole) as the content of β-chloro-*t*-amyl alcohol. Likewise, fraction 3 (19.5%Cl) was found to contain ~67% w. (0.014 mole) of the same alcohol. Further analytical detail is shown below.

Fraction 3 (b.p. 60–108° (115 mm.), $n^{20}\text{D}$ 1.4290, 2.6 g.) was analyzed for water (5.5% w.) and total carbonyl (0.10 equiv./100 g.). One carbonyl was isolated as a reddish-orange 2,4-DNP (dinitrophenylhydrazone), m.p. 175–176°. *Anal.* Calcd. for $C_{11}H_{12}N_4O_4$: C, 50.0; H, 4.7; N, 21.2. Found: C, 50.3; H, 4.8; N, 21.4. Analyses and m.p. are thus in good agreement with the 2,4-DNP of 3-methyl-2-butenal (m.p. 179°).[22] Another minor impurity was 2,2,-5,5-tetramethyltetrahydrofuran—established by g.l.c. correlation with the known compound.

Fraction 4 (b.p. 109–110° (115 mm.), $n^{20}\text{D}$ 1.4427, 5.2 g.) was analyzed for hydroxyl (calcd. for $C_5H_{11}OCl$: 0.82 equiv./100 g.; found: 0.86 equiv./100 g.) and chlorine (24.5%). These data and the infrared analyses indicated a distribution of roughly 17% 2-methyl-2-buten-1-ol and 83% β-chloro-*t*-amyl alcohol. Analysis of combined fractions 4 to 6 (by bromine number) showed the presence of 0.15 mole of double bond/100 g.

Fraction 5 (b.p. 72.5° (11 mm.), $n^{20}\text{D}$ 1.4440, 2.3 g.) gave an infrared spectrum essentially identical with fracton 4. Fraction 6 (b.p. 45° (1 to 2 mm.), $n^{20}\text{D}$ 1.4480, 0.7 g.) was found by infrared analysis to contain some β-chloro-*t*-amyl alcohol (Found: C, 59.9; H, 10.3; Cl, 12.9), but the principal component was not identified conclusively.

Analytical Methods.—The functional groups were determined by conventional methods; gases were analyzed by mass spectrometry.

EMERYVILLE, CALIF.

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[19] L. H. Horsley, *et al.*, "Azeotropic Data," American Chemical Society Publication, Washington, D. C., 1952, p. 28.

[20] Wet carbon analysis was carried out on the extracted inorganic salt phase (after removal of the ether); total of 278 g. at 0.16% w. carbon. Thus, the loss of organic material to this phase is very low.

[21] E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 1148.

[22] E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 500 (1945).

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

Rate Data and Isomer Distribution in the Reaction of Anisole with Mercuric Acetate in Acetic Acid Solution. Partial Rate Factors for the Mercuration Reaction[1-3]

BY HERBERT C. BROWN AND M. DUBECK[4]

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The rate constant for the mercuration of anisole with mercuric acetate in glacial acetic acid is 1.85×10^{-6} l. mole^{-1} sec.$^{-1}$ at 25.0°. Under these conditions substitution occurs 14.0% in the *ortho* and 86% in the *para* position, with no detectable reaction in the *meta* position. These data lead to the partial rate factors: o_f 188 and p_f 2310. The value m_f 1.2 is estimated from the rate constant for *p*-methoxyanisole, 0.634×10^{-5} l. mole^{-1} sec.$^{-1}$. The observed rate constants for *p*-methyl- and *p*-*t*-butylanisole, 0.93 and 1.06×10^{-5} l. mole^{-1} sec.$^{-1}$, are in reasonable agreement with the values calculated from the partial rate factors, 0.58 and 0.88×10^{-5} l. mole^{-1} sec.$^{-1}$, respectively. The rate constants for mercuration of diphenyl ether and acetanilide are 2.67×10^{-6} and 1.91×10^{-6} l. mole^{-1} sec.$^{-1}$, respectively. The available data for the mercuration reaction are correlated with reasonable precision by the electrophilic substituent constants, σ^+.

Previous studies have demonstrated that the available data on electrophilic substitution reactions of toluene[5] and of *t*-butylbenzene[6] are cor-

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[1] Directive Effects in Aromatic Substitution. XLII.

[2] This research supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of the Petroleum Research Fund.

[3] Based upon a thesis submitted by M. Dubeck in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[4] Monsanto Chemical Co. Fellow, 1956–1957.

[5] F. R. Jensen, G. Marino and H. C. Brown, THIS JOURNAL, **81**, 3303 (1959); H. C. Brown and G. Marino, *ibid.*, **81**, 3308 (1959); H. C. Brown, G. Marino and L. M. Stock, *ibid.*, **81**, 3310 (1959); S. U. Choi and H. C. Brown, *ibid.*, **81**, 3315 (1959); H. C. Brown and B. A. Bolto, *ibid.*, **81**, 3320 (1959); L. M. Stock and H. C. Brown, *ibid.*, **81**, 3323 (1959).

[6] (a) H. C. Brown and M. Dubeck, *ibid.*, **81**, 5608 (1959); (b) H. C. Brown and G. Marino, *ibid.*, **81**, 5611 (1959); (c) L. M. Stock and H. C. Brown, *ibid.*, **81**, 5613, 5621 (1959).