# *The Redox Reaction of 1-Ethoxy-n-heptyl Hydroperoxide**

By Shinji MURAI, Noboru SONODA and Shigeru TSUTSUMI

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In our previous study of the redox reaction of an ether-hydroperoxide,[1] we reported that hexane-1, 6-diol diformate and $\gamma$-butyrolactone are produced by the redox reaction of tetrahydrofuran hydroperoxide (a heterocyclic ether hydroperoxide) with ferrous sulfate, and that, in the case of the reaction with cuprous and cupric chlorides, 3-formoxypropyl chloride and $\gamma$-butyrolactone are produced. We then suggested that these products might be formed by carbon-carbon bond fission and carbon-hydrogen bond fission at the $\alpha$-position of the 2-tetrahydrofuranoxy radical generated as an intermediate. The corresponding carbon-oxygen bond fission might lead to the formation of *a carbonyl product*, 4-hydroxybutanal, which was obtained in a trace amount. Now it has become desirable to investigate the redox reaction of the hydroperoxide of a linear ether; therefore, the redox decomposition of 1-ethoxy-*n*-heptyl hydroperoxide (I) has been carried out in order to clarify the nature of these reactions.

## Results and Discussion

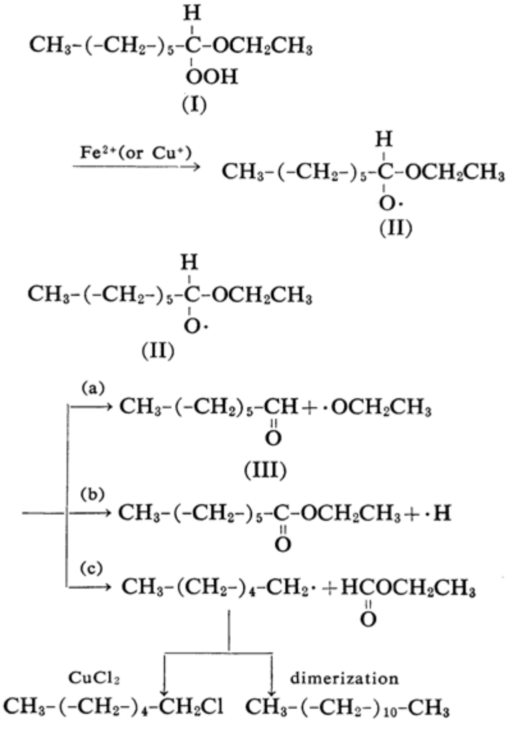
Analytically pure 1-ethoxy-*n*-heptyl hydroperoxide (I) was prepared by the ozonolysis of octene-1 in ethanol. The decomposition reaction of the hydroperoxide (I) was carried out using some metal ions such as ferrous or cuprous ions. When the hydroperoxide I was decomposed in the presence of ferrous sulfate at 7~9°C, ethyl formate, *n*-heptanal, ethyl heptanoate and *n*-dodecane were obtained; they might be formed through the fragmentation of the 1-ethoxy-*n*-heptoxy radical (II) produced by the reductive cleavage of the hydroperoxide I with ferrous ions. In the presence of cupric and cuprous chlorides, the decomposition of I gave ethyl formate, *n*-hexyl chloride, *n*-heptanal and ethyl heptanoate, whereas the formation of *n*-dodecane was not observed because of the chlorination of the *n*-hexyl radical with the cupric chloride used as an alkyl radical scavenger. The *n*-heptanal (III) obtained in both reactions is *the carbonyl product* corresponding to the product which might be given by the carbon-oxygen bond fission of the radical II. However, the mechanism of the carbonyl-product formation is more complicated, as will be discussed later. The results are summarized in Table I.

TABLE I. DECOMPOSITION PRODUCTS OF 1-ETHOXY-*n*-HEPTYL HYDROPEROXIDE

| | Decomposition with $FeSO_4$ Yield, % | Decomposition with $CuCl\text{-}CuCl_2$ Yield, % |
|---|---|---|
| Ethyl formate | 30[a] | 22 |
| *n*-Hexyl chloride | — | 20 |
| *n*-Heptanal | 38 | 26 |
| Ethyl heptanoate | 27 | 26 |
| *n*-Dodecane | 18 | 0 |

a) see Experimental section.

In these reactions, the initial step may be the reductive cleavage of the hydroperoxide I to yield the radical II, which would then react according to the following scheme:



$$\underset{\text{(I)}}{\mathrm{CH_3\text{-}(\text{-}CH_2\text{-})_5\text{-}\overset{H}{\underset{OOH}{C}}\text{-}OCH_2CH_3}} \xrightarrow{\mathrm{Fe^{2+}(or\ Cu^{+})}} \underset{\text{(II)}}{\mathrm{CH_3\text{-}(\text{-}CH_2\text{-})_5\text{-}\overset{H}{\underset{O\cdot}{C}}\text{-}OCH_2CH_3}}$$

$$\underset{\text{(II)}}{\mathrm{CH_3\text{-}(\text{-}CH_2\text{-})_5\text{-}\overset{H}{\underset{O\cdot}{C}}\text{-}OCH_2CH_3}}$$

$$\xrightarrow{\text{(a)}} \underset{\text{(III)}}{\mathrm{CH_3\text{-}(\text{-}CH_2)_5\text{-}\underset{O}{\underset{\Vert}{C}}H}} + \mathrm{\cdot OCH_2CH_3}$$

$$\xrightarrow{\text{(b)}} \mathrm{CH_3\text{-}(\text{-}CH_2\text{-})_5\text{-}\underset{O}{\underset{\Vert}{C}}\text{-}OCH_2CH_3} + \mathrm{\cdot H}$$

$$\xrightarrow{\text{(c)}} \mathrm{CH_3\text{-}(CH_2\text{-})_4\text{-}CH_2\cdot} + \mathrm{H\underset{O}{\underset{\Vert}{C}}OCH_2CH_3}$$

$$\mathrm{CH_3\text{-}(CH_2\text{-})_4\text{-}CH_2\cdot} \xrightarrow{\mathrm{CuCl_2}} \mathrm{CH_3\text{-}(\text{-}CH_2\text{-})_4\text{-}CH_2Cl} \qquad \xrightarrow{\text{dimerization}} \mathrm{CH_3\text{-}(\text{-}CH_2\text{-})_{10}\text{-}CH_3}$$

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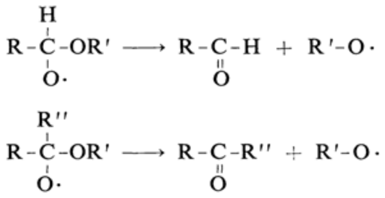
* Presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

[1] S. Murai, N. Sonoda and S. Tsutsumi, This Bulletin, **36**, 527 (1963).

In these reactions, path a comprises the homolytic cleavage of the carbon-oxygen bond, while paths b and c also comprise the fission of the carbon-hydrogen bond and of the carbon-carbon bond of the radical II respectively. The *n*-hexyl radical produced in path c would dimerize to produce *n*-dodecane and also would give *n*-hexyl chloride in the presence of cupric chloride used as an alkyl radical scavenger.

Little attention has been paid to the formation of carbonyl products, aldehydes or ketones in the redox decomposition of the ether-hydroperoxides.

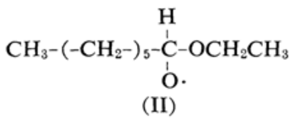


$$R\text{-}\overset{\displaystyle H}{\underset{\displaystyle O\cdot}{C}}\text{-}OR' \longrightarrow R\text{-}\underset{\displaystyle O}{\overset{\|}{C}}\text{-}H + R'\text{-}O\cdot$$

$$R\text{-}\overset{\displaystyle R''}{\underset{\displaystyle O\cdot}{C}}\text{-}OR' \longrightarrow R\text{-}\underset{\displaystyle O}{\overset{\|}{C}}\text{-}R'' + R'\text{-}O\cdot$$

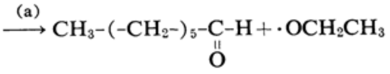
In some cases the hydroperoxides were prepared from carbonyl compounds or ethers and were subjected to reaction without isolation; thus, it was more difficult to clarify the formation of carbonyl products in the redox reaction, and in other cases no effort was made to detect them.[2] Sharp and Patrick reported the formation of aldehydes in a small amount in the ferrous ion-catalyzed decomposition of ether-hydroperoxides.[3] However, the hydroperoxides were not reacted in isolation and were reacted at a rather high temperature, which would induce thermal decomposition. Milas et al. suggested[4] the possible formation of 2-hydroxytetrahydropyran[5] in the ferrous ion-catalyzed decomposition of 2-hydroperoxytetrahydropyran, but the formation of this compound was not reported in a recent investigation of this same system.[6]

In contrast with these results, a rather large amount of a carbonyl compound, *n*-heptanal, was obtained in the present experiment. Some possible reaction pathways for the formation of *n*-heptanal (III) are:



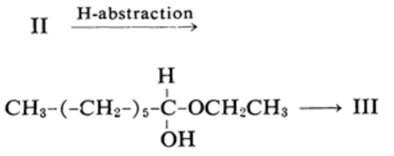
$$CH_3\text{-}(\text{-}CH_2\text{-})_5\text{-}\overset{\displaystyle H}{\underset{\displaystyle O\cdot}{C}}\text{-}OCH_2CH_3$$

(II)



$$\xrightarrow{(a)} CH_3\text{-}(\text{-}CH_2\text{-})_5\text{-}\underset{\displaystyle O}{\overset{\|}{C}}\text{-}H + \cdot OCH_2CH_3$$

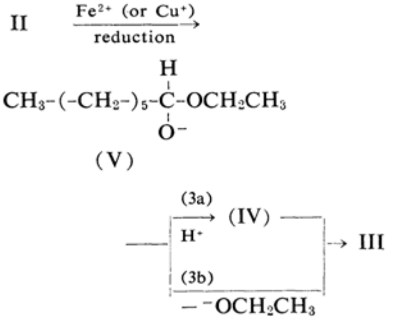
(III) (1)



$$\text{II} \xrightarrow{\text{H-abstraction}}$$

$$CH_3\text{-}(\text{-}CH_2\text{-})_5\text{-}\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}\text{-}OCH_2CH_3 \longrightarrow \text{III} \qquad (2)$$

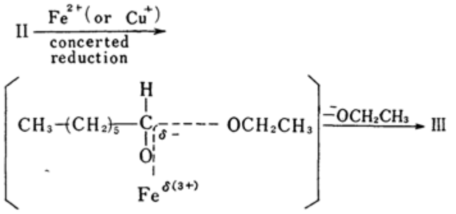
(IV)



$$\text{II} \xrightarrow[\text{reduction}]{Fe^{2+}\text{ (or }Cu^{+})}$$

$$CH_3\text{-}(\text{-}CH_2\text{-})_5\text{-}\overset{\displaystyle H}{\underset{\displaystyle O^-}{C}}\text{-}OCH_2CH_3$$

$$(\text{V}) \left\{\begin{array}{l} \xrightarrow[H^+]{(3a)} (\text{IV}) \\ \xrightarrow{(3b)} -\,^-OCH_2CH_3 \end{array}\right\} \longrightarrow \text{III} \qquad (3)$$



$$\text{II} \xrightarrow[\substack{\text{concerted}\\ \text{reduction}}]{Fe^{2+}(\text{or }Cu^{+})} \left[ CH_3\text{-}(CH_2)_5\text{-}\overset{\displaystyle H}{\underset{\substack{O\\ |\\ Fe^{\delta(3+)}}}{C^{\delta-}}}\text{-----}OCH_2CH_3 \right] \xrightarrow{^-OCH_2CH_3} \text{III}$$

(VI) (4)

It may be assumed that the pathway shown by Eq. 4 is the most plausible from the following consideration; since the transition state for the homolytic cleavage of an alkoxy radical involves the stretching of the breaking bond, the free energy of the activation for the cleavage would be expected to be raised as the stability of the leaving radical is decreased. Therefore, the homolytic cleavage of the carbon-oxygen bond, Eq. 1, would be unable to compete with the carbon-carbon bond cleavage (step c) or the carbon-hydrogen bond cleavage (step b) because of the relative instability of the leaving ethoxy radical. Furthermore, as to Eq. 2, there may exist a few hydrogen donors for H-abstraction except the hydroperoxide itself and its decomposition products, which may be insufficient in amount to serve efficiently. Equation 3 shows the reduction of the alkoxy radical II to the corresponding anion V, followed by the protonation 3a or by the leaving of the ethoxide ion 3b. Such a reduction of an alkoxy radical with reducing metal ions has been reported by Kochi.[7]

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[2] For example, a) J. K. Kochi and F. F. Rust, *J. Am. Chem. Soc.*, **84**, 3946 (1962); b) R. V. Digman and D. F. Anderson, *J. Org. Chem.*, **28**, 239 (1963).

[3] D. B. Sharp and T. M. Patrick, Jr., *J. Org. Chem.*, **26**, 1389 (1961).

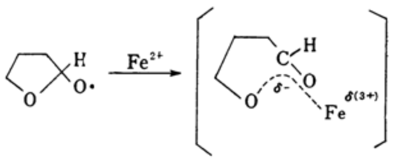
[4] N. A. Milas, R. L. Peeler, Jr., and O. L. Mageli, *J. Am. Chem. Soc.*, **76**, 2322 (1954).

[5] This compound is in equilibrium with 5-hydroxypentanal and corresponds to the carbonyl product.

[6] E. A. Youngman, F. F. Rust, G. M. Coppinger and H. E. De La Mare, *J. Org. Chem.*, **28**, 144 (1963).

[7] J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 1193 (1962).

Equation 3, however, cannot explain the different results that, in the present reaction of the hydroperoxide of the linear ether, a carbonyl product was obtained in a better yield than in the case of the cyclic ether system reported on previously.[1] This result may be explained most reasonably in terms of the concerted reduction, Eq. 4, in which the partial breaking of the carbon-oxygen bond might be more sterically favorable in the transition state VI than in a cyclic ether system VIII.



(VIII)

⟶ 4-Hydroxybutanol

Because of the reasons described above, it seems reasonable to assume that *n*-heptanal is produced by the reduction of radical II with ferrous or cuprous ions, followed concertedly by the leaving of the ethoxide ion, which may be a suitable leaving anion.

There assumptions are also supported by the fact that cyclohexanone was generated as a carbonyl product in the redox reaction of 1-ethoxycyclohexyl hydroperoxide under the same conditions as is described above.[8]

## Experimental

**1-Ethoxy-*n*-heptyl Hydroperoxide (I).** — Eighteen grams of 1-octene was dissolved in 350 ml. of ethanol, and a stream of ozone containing oxygen was passed at −70°C until the completion of the reaction was indicated by the liberation of iodine in an aqueous solution of potassium iodide at the gas outlet. The solvent and the cleavaged fragment were removed under reduced pressure at room temperature, and then further removed in vacuo (0.5 mmHg) at room temperature for three hours. The residual colorless oil (26 g.) showed infrared absorptions at 3400 cm$^{-1}$ (-OH) and 1100 cm$^{-1}$ (C-O-C) and reacted positively to a lead tetraacetate test. The amount of active oxygen was determined by iodometry to be 9.27% (Calcd. for $C_9H_{20}O_3$ : 9.08%). Molecular weight (in benzene) 180 (Calcd. for $C_9H_{20}O_3$ : 176.3%).

**The Reaction of 1-Ethoxy-*n*-heptyl Hydroperoxide (I) with Ferrous Sulfate.**—Into a solution of 15.0 g. of ferrous sulfate heptahydrate in 70 ml. of water 8.0 g. of the hydroperoxide I was vigorously stirred, drop by drop, over a period of 20 min. at 7∼9°C. The stirring was then continued for a further three hours at a room temperature. From the reaction mixture a low boiling material was distilled out directly, at room temperature and at 10 mmHg, in to a trap cooled at −70°C.

After the removal of water from this trap by a separatory funnel, 1.1 g. of ethyl formate was obtained. By gas chromatographic analysis this fraction was shown to contain a small amount of *n*-hexane and hexene-1, but no effort was made to make a quantitative determination of these compounds.

The reaction mixture, after the removal of the low boiling material, was extracted with five 100 ml. portions of ether. The ether extract was dried over anhydrous magnesium sulfate. The evaporation of the ether gave 6.0 g. of products which were estimated by gas chromatography to contain 2.2 g. of *n*-heptanal, 2.3 g. of ethyl heptanoate and 1.5 g. of *n*-dodecane; column, Silicon DC-550 and PEG 6000; column temperature, 130°C; carrier gas, $H_2$. The 2, 4-dinitrophenylhydrazone of *n*-heptanal was prepared by treating the above-mentioned reaction mixture with a hydrochloric acid solution of 2, 4-dinitrophenylhydrazine; its melting point and mixed melting point with an authentic sample were each 108∼109°C.

**The Reaction of 1-Ethoxy-*n*-heptyl Hydroperoxide (I) with Cuprous Chloride and Cupric Chloride.**—Into a suspension of 5.0 g. of cuprous chloride and 8.8 g. of cupric chloride dihydrate in 100 ml. of water 8.0 g. of the hydroperoxide I was vigorously stirred, drop by drop, over a period of 30 min. at 5∼7°C. The stirring was then continued for a further three hours. The reaction mixture was treated in the manner mentioned above. From the low boiling product, 0.7 g. of ethyl formate, and from the ether extract, 1.0 g. of *n*-hexyl chloride, 1.5 g. of *n*-heptanal and 2.1 g. of ethyl heptanoate were obtained, although no formation of *n*-dodecane was observed by gas chromatographic analysis.

## Summary

1) The reaction of 1-ethoxy-*n*-heptyl hydroperoxide with ferrous sulfate has given ethyl formate, *n*-heptanal, ethyl heptanoate and *n*-dodecane, while the reaction with a mixture of cuprous and cupric chlorides has given ethyl formate, *n*-hexyl chloride, *n*-heptanal and ethyl heptanoate.

2) The formation of *n*-heptanal in both reactions has been attributed to the reduction of the 1-ethoxy-*n*-heptanoxy radical with ferrous or cuprous ions to the corresponding anion, followed concertedly by the leaving of the ethoxide ion.

3) The probable reaction pathway, especially the difference between the natures of the heterocyclic ether syetem and the linear ether system, has been discussed.

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[8] S. Murai, N. Sonoda and S. Tsutsumi, unpublished work: Analytically pure 1-ethoxycyclohexyl hydroperoxide was prepared by the ozonolysis of methylenecyclohexane in ethanol; b. p. 50∼58°C (ca. $10^{-2}$ mmHg); $n_D^{20}$, 1.4602.

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*Department of Chemical Technology*
*Faculty of Engineering*
*Osaka University*
*Miyakojima-ku, Osaka*