Redox Reaction of Tetrahydrofuran Hydroperoxide

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The hydroperoxides of various ethers have been synthesized and their decomposition reactions have been reported by several workers$^{1)}$. There have been little reports, however, on the redox reaction of the ether hydroperoxide$^{2,3)}$. This investigation was carried out to clarify the nature of the reaction of an ether hydroperoxide, and tetrahydrofuran hydroperoxide (THF-HPO) was used as a starting material since it is readily available by the autoxidation of tetrahydrofuran$^{4)}$ and can be handled without any explosion. The decomposition reaction of THF-HPO was carried out by using some metal ions such as ferrous or cuprous ion.

Results

THF-HPO was decomposed in the presence of ferrous sulfate at $-2\sim3°C$, and hexane-1,6-diol-diformate (I) and γ-butyrolactone (II) were obtained as the main products, and a small amount of 4-hydroxybutanal (III) was isolated as its 2, 4-dinitrophenylhydrazone derivative. Hexane-1, 6-diol-diformate (I) might be formed by the dimerization of 3-formoxypropyl radical (IV) produced through the β-fission of the carbon-carbon bond of 2-tetrahydrofuranoxy radical (V).

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1) a) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides", Intersicence Pub. Inc., New York, N. Y. (1954); b) A. G. Davies, "Organic Peroxides", Butterworths Pub. Inc. London (1961). There are many other books and reviews.

2) J. Kumamoto, H. E. De La Mare and F. F. Rust, *J. Am. Chem. Soc.*, **82**, 1935 (1960).

3) D. B. Sahrp and T. M. Patrick, *J. Org. Chem.*, **26**, 1389 (1961).

4) H. Rein and R. Criegee, *Angew. Chem.*, **62**, 120 (1950).

TABLE I. REACTION OF THF-HPO WITH FERROUS SULFATE

Exp. No.	Reagent		Product[a)]		
	THF-HPO g. (mol.)	$FeSO_4 \cdot 7H_2O$ g. (mol.)	Hexane-1, 6-diol-diformate (I) g. (mol.), yield, %	γ-Butyrolactone- (II) g. (mol.), yield, %	4-Hydroxy-butanal (III)[b)]
1	10.4(0.10)	27.8(0.10)	1.2(0.007) 13.8	2.7(0.031) 31.4	trace

TABLE II. REACTION OF THF-HPO WITH METAL HALIDES

Exp. No.	Reagent				Product[a)]		
	THF-HPO g. (mol.)	CuCl g. (mol.)	$CuCl_2 \cdot 2H_2O$ g. (mol.)	NaCl g. (mol.)	3-Formoxypropyl-chloride (VI) g. (mol.), yield, %	γ-Butyro-lactone (II) g. (mol.), yield, %	4-Hydroxy-butanal (III)[b)]
2	13.6(0.13)	12.9(0.13)	22.1(0.13)	—	6.7(0.0055) 42.3	1.9(0.0022) 16.9	trace
3	6.0(0.058)	5.7(0.058)	—	3.4(0.058)	1.7(0.0014) 24.6	1.8(0.0021) 36.8	trace
4	9.0(0.087)	8.6(0.087)	—	—	2.3(0.0019) 21.8	0.7(0.0008) 9.2	trace

a) The yields were calculated from the gas chromatographic analysis of crude products[9)].

b) The yields of this product was estimated as less than 1.0 wt. % by the gravimetric determination of its 2, 4-dinitrophenylhydrazone derivative.

In the presence of metal halide, the dimerization of 3-formoxypropyl radical (IV) was not observed, and halogen derivative, trapped by halogen, was obtained as the main product instead of the dimer. For example, when THF-HPO was added to the suspension mixture of cuprous chloride and cupric chloride in water at 0~5°C, 3-formoxypropyl chloride (VI) was produced in a yield of 42.3% being accompanied by γ-butyrolactone (II) (16.9%) and a trace amount of 4-hydroxybutanal (III). The results obtained are summerized in Tables I and II.

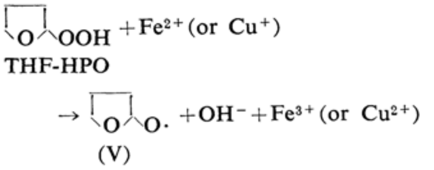
Discussion

A hydroperoxide may decompose in a number of different ways when treated with metal ions having variable oxidation numbers. Equations 1 and 2 would be possible in the reaction of hydroperoxide with ferrous (or cuprous) and ferric (or cupric) ions respectively as the first step of the redox reaction.

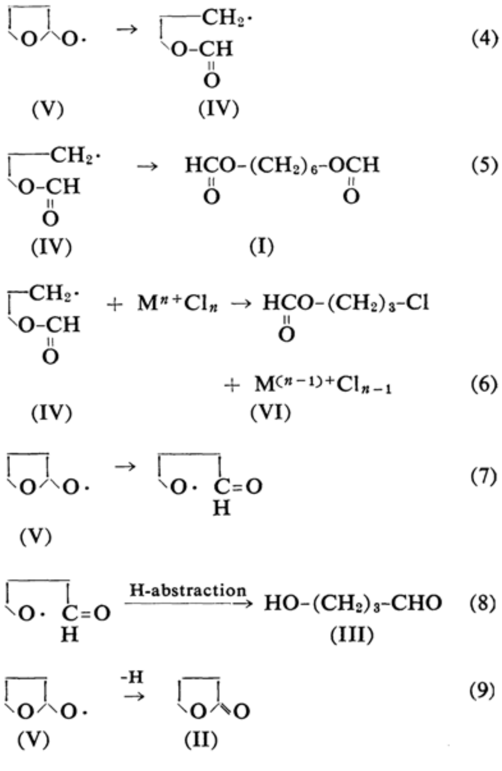
$$\mathrm{ROOH} + \mathrm{Fe}^{2+}\,(\text{or } \mathrm{Cu}^{+}) \rightarrow \mathrm{RO}\cdot + \mathrm{OH}^{-} + \mathrm{Fe}^{3+}\,(\text{or } \mathrm{Cu}^{2+}) \qquad (1)$$

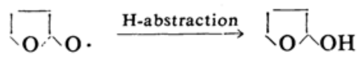
$$\mathrm{ROOH} + \mathrm{Fe}^{3+}\,(\text{or } \mathrm{Cu}^{2+}) \rightarrow \mathrm{ROO}\cdot + \mathrm{H}^{+} + \mathrm{Fe}^{2+}\,(\text{or } \mathrm{Cu}^{+}) \qquad (2)$$

Equation 1 shows a reaction of a hydroperoxide with a metal ion in its lower oxidation state, such as ferrous (or cuprous) ion, and Eq. 2 shows the reaction with a metal ion in its higher oxidation state. At the reaction temperature of −3~5°C, used in these experiments, the reaction 1 may be preferable from the fact that no reaction was observed between THF-HPO and cupric chloride in water solution below 5°C. Thus, 2-tetrahydrofuranoxy radical (V) seems to be produced as the first step of these reactions.



Several reactions of the radical V would be probable as shown below.





(V) (VII) (10)

Equations 4, 7 and 9 show the β-fission of the carbon-carbon, carbon-oxygen and carbon-hydrogen bonds of the 2-tetrahydrofuranoxy radical (V) respectively. Equation 10 is the hydrogen abstraction of the 2-tetrahydrofuranoxy radical (V), giving 2-tetrahydrofuranol (VII).

The 3-formoxypropyl radical (IV) produced in the reaction 4 would dimerize to hexane-1, 6-diol-diformate (I) as shown by Eq. 5. On the other hand, in the presence of additives such as copper chloride, the 3-formoxypropyl radical (IV) gave 3-formoxypropyl chloride (VI) through the path of Eq. 6.

There may be some plausible explanations for such chlorination process. Kumamoto and his coworkers²⁾ have suggested that the chlorination process is best explicable by chlorine-bridged transition state in which chlorine is transferred to an alkyl radical.

$$R\cdot + M^{n+}Cl_n \rightarrow [R\cdots Cl\cdots M^{n+}Cl_{n-1}]$$
$$\rightarrow RCl + M^{(n-1)+}Cl_{n-1}$$

Recently Minisci⁵⁾ has reported the reaction of carbon free radical with some metallic salts and pointed out that such a process may be interpreted by the analogous to that of Sandmeyer's reaction presented by Waters⁶⁾. Kochi⁷⁾ has postulated that such a transition state for redox reaction can be well represented as a resonance hybrid between ligand transfer and electron transfer contribution.

$$[R{-}ClM^{+(n-1)} \leftrightarrow R\cdot Cl{-}M^{+n}$$
$$\leftrightarrow R^{\oplus}Cl{-}M^{+(n-1)}]$$

It is considered that the reaction of 3-formoxypropyl radical (IV) would also proceed via the reaction process described above, and dimerization would be inhibited by the more favorable chlorine transfer process.

The reaction 9 gave γ-butyrolactone (II). It might be possible, however, that II was produced through a rather ionic process.

As shown in Eqs. 7 and 8, the product obtained by carbon-oxygen bond fission of 2-tetrahydrofuranoxy radical (V) is 4-hydroxybutanal (III) which is under equilibrium with 2-tetrahydrofuranol (VII). As mentioned above 2-tetrahydrofuranol is also obtained by Eq. 10. The yield of this product is very low and estimated to be less than 1.0 wt. % by 2, 4-dinitrophenylhydrazone gravimetric method. It seems to us from these results that carbon-oxygen bond fission or hydrogen abstraction is more difficult to occur than carbon-carbon or carbon-hydrogen bond fission under these experimental conditions.

From the results of experiments 3 and 4, it is inferred that the addition of chlorine anion has no apparent effect on the yield of 3-formoxypropyl chloride (VI).

Experimental

Material.—THF-HPO⁴⁾ used was synthesized by autoxydation of THF at 45°C according to Rein's method. About 20 g. of THF-HPO was obtained from 400 ml. of THF and was purified by distillation, b. p. 40°C/0.2 mmHg. The amount of active oxygen was determined by iodometry, 15.3∼15.4% (Calcd. for $C_4H_8O_3$: 15.4%).

Reaction of THF-HPO with Ferrous Sulfate (Exp. 1).—To a solution of 27.8 g. of ferrous sulfate heptahydrate in 100 ml. of water was added 10.4 g. of THF-HPO dropwise over the period of 30 min. at −2∼3°C under vigorous stirring. The reaction mixture was extracted with ether, and then the extract was dried over anhydrous magnesium sulfate. After the ether was evaporated, the residue was devided into the following two fractions, fraction 1, 2.7 g. of colorless oily liquid: b. p. 102∼105°C/27 mmHg, fraction 2, 1.2 g. of colorless oily liquid: b. p. 137∼139°C/27 mmHg.

The infrared spectrum of the fraction 1 showed strong bands at 1771 (C=O of lactone) and 1169 cm⁻¹ (C-O-C), and was identical with that of γ-butyrolactone (II). This fraction 1 was also identified as II by gas chromatography: column, Silicone DC-550, DNP and PEG; column temperature, 140°C; carrier gas, H_2. The fraction 1 contained 3.7 wt. % of 4-hydroxybutanal (III) identified and determined as its 2, 4-dinitrophenylhydrazone derivative: m. p. 114∼115°C (lit.⁸⁾ m. p. 116∼117°C).

Found: C, 45.44; H, 4.86. Calcd. for $C_{10}H_{12}O_5N_4$: C, 44.78; H, 4.51%.

The fraction 2, b. p. 137∼139°C/27 mmHg, was purified by redistillation and showed an identical infrared spectrum with that of an authentic sample of hexane-1, 6-diol-diformate (I): 1720 (C=O) and 1180 cm⁻¹ (C-O-C).

Found: C, 55.10; H, 8.12. Calcd. for $C_8H_{14}O_4$: C, 55.16; H, 8.10%.

Reaction of THF-HPO with Cuprous Chloride and Cupric Chloride (Exp. 2).—To the suspension mixture of 12.9 g. of cuprous chloride and 22.1 g. of cupric chloride dihydrate in 100 ml. of water was added dropwise 13.6 g. of THF-HPO over the period of 30 min. under vigorous stirring at 0∼5°C. After the reaction mixture was extracted with ether, the ether extract was dried over anhydrous magnesium sulfate, and the ether was removed, and then the residue was separated into two components by the preparative gas chromatography: type, Yanagimoto G. C. G-2, No. 214; column, Silicone DC-550; column temperature, 141.5°C; carrier gas, N_2. The two components were redistilled respectively, fraction 3 of b. p. 65∼66°C/27 mmHg and fraction

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5) F. Minisci, R. Galli, *Tetrahedron Letters*, p. 533 (1962).

6) D. C. Nonhebel and W. A. Waters, *Proc. Roy. Soc.*, **A242**, 16 (1957).

7) J. K. Kochi, *Tetrahedron*, **18**, 483 (1962).

8) C. L. Wilson, *J. Chem. Soc.*, **1945**, 52.

4 of b. p. 100∼105°C/27 mmHg. The fraction 4 was identified as II by gas chromatographic analysis⁹⁾. The infrared spectrum of fraction 3 showed strong absorption bands at 1718 (C=O) and 1180 cm^{-1} (C-O-C) and was identical with that of an authentic sample of 3-formoxypropyl chloride (VI). It shows the same retention time as that of an authentic sample in the gas chromatographic analysis⁹⁾. α-Naphthylurethan derivative of its hydrolysis product, 3-hydroxypropyl chloride, was prepared and mixed melting point with an authentic sample was not depressed, m. p. 76.2∼77.2°C.

Found: C, 63.46; H, 5.28. Calcd. for $C_{14}H_{14}O_2 \cdot NCl$: C, 63.76; H, 5.35%.

From the gas chromatographic analysis⁹⁾, 8.4 g. of the crude distillate of b. p. 65∼102°C/27 mmHg was estimated to contain 6.7 g. of VI and 1.9 g. of II. Compound III was identified and estimated as less than 1.0 wt. % of the crude fraction in the same manner as used in Exp. 1.

Reaction of THF-HPO with Cuprous Chloride and Sodium Chloride (Exp. 3).—To the suspension mixture of 5.7 g. of cuprous chloride and 3.4 g. of sodium chloride in 50 ml. of water was added 6.0 g of THF-HPO at 3∼5°C over the period of 25 min. The reaction mixture was treated in the same manner as used above and 3.5 g. of a fraction of b. p. 65∼120°C/23 mmHg was obtained. This fraction was estimated to contain 1.7 g. of VI and 1.8 g. of II from the gas chromatographic analysis⁹⁾, and also contained a trace of III estimated as less than 1.0 wt. % of this fraction.

Reaction of THF-HPO with Cuprous Chloride (Exp. 4).—To the 8.6 g. of cuprous chloride in 70 ml. of water was added 9.0 g. of THF-HPO at 0∼5°C. From the reaction mixture, 3.0 g. of a fraction of b. p. 59∼95°C/19 mmHg was obtained. From the gas chromatographic analysis⁹⁾, this fraction included 2.3 g. of VI and 0.7 g. of II, and also contained a trace of III identified as its 2, 4-dinitrophenylhydrazone (less than 1.0 wt. % of this fraction).

Summary

1) Reaction of tetrahydrofuran hydroperoxide with ferrous sulfate produced hexane-1, 6-diol-diformate (13.8%), which was formed by the dimerization of 3-formoxypropyl radical generated from 2-tetrahydrofuranoxy radical, and γ-butyrolactone (31.4%) and 4-hydroxybutanal (trace).

2) In the presence of metal halide, the dimerization of the 3-formoxypropyl radical did not occur and halogenation of the 3-formoxypropyl radical was observed. For example, when tetrahydrofuran hydroperoxide was reacted with cuprous chloride and cupric chloride, 3-formoxypropyl chloride was obtained in a yield of 42.3%.

3) It is worth nothing that under suitable experimental condition the chloro compound was obtained in a good yield.

4) Probable reaction process was discussed.

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9) The qualitative and quantative estimations were carried out under the following condition; column, Silicon DC-550; column temperature, 140°C; carrier gas, H_2.