

Reaction of Sulfides with *t*-Butyl Hypochlorite in the Presence of Water, ^{18}O Tracer Study

Kunihiro KIKUKAWA, Waichiro TAGAKI, NORIO KUNIEDA and Shigeru OAE

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto-cho, Sumiyoshi-ku, Osaka

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It has been found that *t*-butyl hypochlorite oxidizes organic sulfides to the corresponding sulfoxides or sulfones under suitable reaction conditions, and the synthetic utility of this oxidation to prepare sulfoxide has been examined for series of sulfides.¹⁻⁴ However, the mechanistic features have not been fully explored yet. Skell and Epstein obtained sulfoxides by the oxidation of corresponding sulfides at low temperature (-78°C) and suggested the following mechanism (Eq. (1)) which involves an alkoxy sulfonium salt as the intermediate. Walling and Mintz carried out the same reaction in benzene at room temperature, and found that the stoichiometry of the reaction was not 1 : 1 with respect to both the sulfide and the reagent as



would be expected from Eq. (1), but the ratio was 1 : 2 and a high yield of sulfoxide and a mixture of products from hypochlorite were obtained. They did not observe any sulfone formation contrary to other reports,² and suggested a polar mechanism involving molecular chlorine and diphenyl sulfur dichloride for oxidation of diphenyl sulfide, rejecting free radical mechanisms.

During the courses of our investigation on the oxidation of organic sulfur compounds with halogenating agents, we have been interested in the

fate of oxygen atom in the above oxidation. It is obvious that the oxygen atom of the sulfoxide must come from *t*-butyl hypochlorite when the reaction is carried out in non-hydroxylic solvent. Meanwhile, it has been reported that in the presence of water molecular halogen oxidizes sulfides to the corresponding sulfoxides.⁵⁻⁷ In this oxidation, ^{18}O tracer experiments have demonstrated that the oxygen atom of the sulfoxide comes exclusively from water, and not from any other solvent components such as acetic acid or methanol, etc.⁷ However, the last possibility of oxygen uptake into sulfoxide from other solvents cannot still be ruled out in some other system.⁸

Therefore, it is interesting to examine the effect of water on the above *t*-butyl hypochlorite oxidation.

Results and Discussion

Oxidation of diphenyl sulfide with an equimolar amount of *t*-butyl hypochlorite in dioxane at room temperature yielded the corresponding sulfoxide. Any intermediate, such as that isolated by Skell and Epstein² at low temperature, was not observed.

5) W. Ranky and D. Nelson, "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, Inc, New York, N. Y. (1961), p. 170.

6) H. Szmant, Ref. 5, p. 154.

7) S. Oae, Y. Ohnishi, S. Kozuka and W. Tagaki, This Bulletin, **39**, 364 (1966) and the related papers.

8) For example, recently Higuchi has shown that in the iodine oxidation of sulfide to give sulfoxide, phosphate and carboxylate anion are effective catalysts, presumably by forming unstable sulfonium intermediate which could decompose to give unlabeled sulfoxide (T. Higuchi and K.-H. Gensch, *J. Am. Chem. Soc.*, **88**, 5486 (1966)).

1) R. J. Gritter and D. J. Carey, *J. Org. Chem.*, **29**, 1160 (1964).

2) P. S. Skell and M. F. Epstein, Abstracts 147th National Meeting of American Chemical Society (Philadelphia, Pa., April 1964,) p. 26N.

3) C. Walling and M. J. Mintz, *J. Org. Chem.*, **32**, 1286 (1967).

4) L. Skattebøl, B. Boulette and S. Solomon, *J. Org. Chem.*, **32**, 3111 (1967).

TABLE 1. OXIDATION OF DIPHENYL SULFIDE WITH *t*-BUTYL HYPOCHLORITE

Mole ratio ^{a)} I : II : III	Yield, %		¹⁸ O atom %		
	IV	V	III	IV	V
1 : 1 : 2	60	—	1.72	1.14	—
1 : 2 : 2	—	80	1.72	—	1.37
1 : 2 : 10	—	90	1.62	—	1.62

a) One gram of I in 30 ml of the mixture of II and III.

With twice molar amounts of hypochlorite, diphenyl sulfone was obtained as the main product. The addition of water to the reaction mixture did not change the product composition. The possibility of ¹⁸O (of water) incorporation into the products was then examined. The results summarized in Table 1 shows that the ¹⁸O incorporation did take place in both sulfoxide and sulfone formation. The amount of incorporation was more than 80% and approached 100% as the amount of water increased. The ¹⁸O incorporation has been also examined for the oxidation of sulfoxide to the corresponding sulfone. As shown in Table 2, the oxygen atom of water was again found to be incorporated in the sulfone.

TABLE 2. OXIDATION OF DIPHENYL SULFOXIDE WITH *t*-BUTYL HYPOCHLORITE

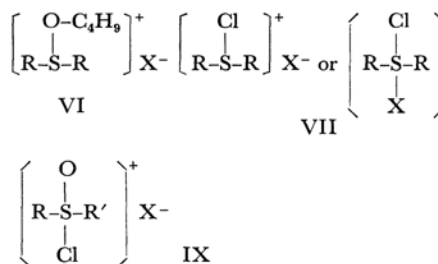
Atom % of ¹⁸ O in ^{a)}		
Water	Sulfoxide	Sulfone
0.20	1.02	0.62
1.60	1.02	1.25
1.60	0.21	0.78

a) Mole of ratio of sulfoxide : *t*-C₄H₉OCl : H₂O = 1 : 2 : 2

The formation of ¹⁸O labeled sulfoxide does not necessarily rule out the possibility that the primary product is the unlabeled sulfoxide which then undergoes an oxygen exchange reaction catalyzed by the hydrogen chloride formed.⁹⁾ Therefore, the oxygen exchange reaction of diphenyl sulfoxide was examined by adding hydrogen chloride

instead of adding *t*-butyl hypochlorite, although the results in Table 2 indicate that such oxygen exchange reaction must be slow compared to the oxidation reaction. This control experiment also reveals that the oxygen exchange of a sulfoxide is negligible under these conditions (see Experimental).

The above oxidation reaction presumably proceeds through the hydrolysis of either one of the following two different intermediates, VI or VII. For the hydrolysis of VI, there are two possibilities, *i. e.* one is the attack of water on the sulfur atom giving a labeled sulfoxide, the other is the solvolysis of *t*-butyl group giving an unlabeled sulfoxide. The



attack of chloride anion on *t*-butyl group would also give an unlabeled sulfoxide. This possibility, however, is not in accord with the above experimental results. Meanwhile it is difficult to consider that the nucleophilic reaction takes place exclusively on the sulfur atom rather than on *t*-butyl group. Therefore, the more likely intermediate is VII which rapidly reacts with water to give a sulfoxide. In the absence of water *t*-butoxy anion would react with VII to give VI. The formation of VI and its decomposition to give the sulfoxide would be slower than the formation of VII and its hydrolysis.

The formation of the sulfone and the incorporation of ¹⁸O into the sulfone with identical concentration as that of the sulfoxide seem to suggest that the chlorosulfoxonium (IX) is formed as the intermediate which upon quenching with water is converted to the sulfone.

Experimental

Materials. Dioxane was purified by treating with hydrochloric acid and with metallic sodium. Diphenyl sulfide was prepared by Friedel-Crafts reaction of benzene and elemental sulfur according to the method used by Dougherty and Hammond.¹⁰⁾ Diphenyl sulfoxide was prepared by the oxidation of diphenyl sulfide with hydrogen peroxide. *t*-Butyl hypochlorite was prepared by the reaction of *t*-butanol with chlorine in a sodium hydroxide solution according to the method of Leeter and Bell.¹¹⁾ Diphenyl sulfoxide ¹⁸O-labeled was prepared by the oxidation of diphenyl sulfide in a mixture of

9) a) K. Mislow, T. Simmons, J. T. Mellilo and A. L. Ternay, *J. Am. Chem. Soc.*, **86**, 1452 (1964). b) K. Kikukawa, W. Tagaki, N. Kunieda and S. Oae, *This Bulletin*, **39**, 614 (1966).

10) G. Dougherty and P. D. Hammond, *J. Am. Chem. Soc.*, **57**, 117 (1935).

11) H. M. Leeter and E. W. Bell, "Org. Synth.," Coll. Vol. IV, p. 125 (1963).

bromine- H_2^{18}O -pyridine.⁷⁾

Oxidation of Diphenyl Sulfoxide and Sulfone with *t*-Butyl Hypochlorite in ^{18}O Enriched Water-Dioxane. To a solution of diphenyl sulfoxide in dioxane-water was added *t*-butyl hypochlorite dropwise under stirring at 15°C. After one hour, most of the solvent was removed by concentration under reduced pressure, and water was added to the residue to give crystalline product. The properties and the purity of diphenyl sulfoxide was discussed in the previous paper.^{8b)} The

results are shown in Tables 1 and 2.

Control Experiment. ^{18}O -Labeled diphenyl sulfoxide was treated under the same reaction conditions as in the above oxidation, except that an equimolar amount of hydrogen chloride was added in place of *t*-butyl hypochlorite.

After one hour, diphenyl sulfoxide was recovered and its ^{18}O content was assayed:

Atom % of ^{18}O : Starting sulfoxide, 0.827; recovered sulfoxide, 0.821.
