

Selective Oxidation of Sulfides to Sulfoxides by a Polymeric Reagent Electrochemically Generated and Recycled *in Situ*

Jun-ichi YOSHIDA, Hiroshi SOFUKU, and Nariyoshi KAWABATA*

Department of Chemistry, Faculty of Polytechnic Science, Kyoto Institute of Technology,
Matsugasaki, Sakyo-ku, Kyoto 606

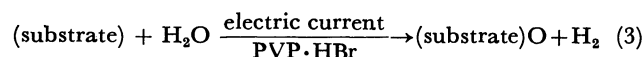
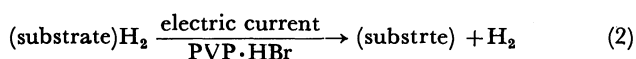
(Received August 11, 1982)

Synopsis. A polymeric reagent electrochemically generated from crosslinked poly(4-vinylpyridine) hydrobromide was found to oxidize sulfides to give sulfoxides in high yields. The exhausted polymeric reagent was regenerated by continuous electrochemical oxidation *in situ*.

Recently we have reported a facile oxidation of alcohols by a polymeric reagent electrochemically generated from crosslinked poly(4-vinylpyridine) hydrobromide (PVP·HBr).^{1,2)} Since the exhausted polymeric reagent is regenerated by continuous electrochemical oxidation *in situ*, the method does not consume any chemical oxidant and does not produce any contaminating reduced product. Based on this methodology, we have begun a program to study the selective oxidation of a variety of functional groups. In this note, we wish to report that the polymeric reagent electrochemically generated from PVP·HBr acts as an effective reagent for the selective oxidation of sulfides to sulfoxides.



In the case of alcohol oxidation, the substrate undergoes a net oxidative dehydrogenation (Eq. 2). The present reaction of sulfides provides another application of the method in which water acts as the primary oxidant in the net sense (Eq. 3).



The sulfide oxidation reaction can be carried out by either the ex-cell method or the in-cell method. In the case of the ex-cell method, the polymeric oxidizing reagent was prepared by passing the electric current (4.5 mF) through PVP·HBr beads (3.00 wet g, containing 5.10 mmol of HBr) in acetonitrile as reported previously.¹⁾ The polymeric reagent was separated by filtration and allowed to react with dibutyl sulfide (2.30 mmol) in acetonitrile at room temperature to afford dibutyl sulfoxide (0.64 mmol).

The in-cell method is more convenient. The electric current was passed through a mixture of a catalytic amount of PVP·HBr, (3.00 wet g) containing 4.94 mmol of HBr, dibutyl sulfide (20.0 mmol) and acetonitrile (3.0 ml) in an undivided cell at 30 °C. After 2.4 F/mol of electricity (based on the sulfide) was passed, GLC analysis of the reaction mixture showed the formation of dibutyl sulfoxide in a quantitative yield. During the course of the reaction hydrogen gas evolved in a quantitative yield, indicating that water acts as a primary oxidant. The result indicates the efficient electrochemical regeneration of the exhausted polymeric reagent *in situ*. After removal of the resin beads by filtration, the product was isolated by bulb-to-bulb distillation (95% yield). The oxidation of other sulfides also proceeded smoothly under the similar conditions to provide the corresponding sulfoxides in good to excellent yields as

TABLE 1. OXIDATION OF SULFIDES BY A POLYMERIC REAGENT ELECTROCHEMICALLY GENERATED AND RECYCLED *in situ*^{a)}

Sulfide	Sulfide/Br ^{-b)}	Electricity F/mol ^{c)}	Product	Yield ^{d)} %
$n\text{-C}_4\text{H}_9\text{SC}_4\text{H}_9\text{-}n$	4.38	2.24	$n\text{-C}_4\text{H}_9\text{S(O)}\text{C}_4\text{H}_9\text{-}n$	95
	4.04	2.40		(100)
		2.38		(100) ^{e)}
		2.40		(100) ^{f)}
	5.17 ^{g)}	2.40		(83) ^{h)}
$n\text{-C}_8\text{H}_{17}\text{SCH}_3$	4.08	2.02	$n\text{-C}_8\text{H}_{17}\text{S(O)}\text{CH}_3$	72
	4.27	2.40		(78)
	3.63	2.04		83
	4.27	2.40		(95)
PhSCH_3	4.07	2.40	$\text{PhS(O)}\text{CH}_3$	86
	4.14	2.20		(96)

a) Reactions were carried out with 20.0 mmol of sulfides and 3.00 wet g of PVP·HBr beads in 3.0 ml of acetonitrile at 30°C. b) The molar ratio of sulfide to the bromide ion contained in PVP·HBr. c) Based on the sulfide. d) Isolated yield, based on the sulfide. Yields determined by GLC analysis are given in parentheses. e) The second use of the resin. f) The third use of the resin. g) PVP·HCl was used instead of PVP·HBr. h) Significant amount of dibutyl sulfone was produced as a by-product.

shown in Table 1.

The resin beads are reusable in the electrochemical oxidation. In this case the resin beads were separated from the reaction mixture by filtration, washed with organic solvents, soaked in water, filtered to remove excess water, and used for the electrochemical oxidation of sulfide. The activity of the resin beads did not decrease after the second use.

It is noteworthy that when crosslinked poly(4-vinylpyridine) hydrochloride (PVP·HCl) was used instead of PVP·HBr, the yield of the sulfoxide was lower and significant amount of the sulfone was produced. Thus, the polymeric reagent electrochemically generated from PVP·HCl has higher oxidizing ability than that from PVP·HBr. This is probably due to the higher oxidation potential of the chloride ion than that of the bromide ion.

Although there are several known procedures for the selective oxidation of sulfides to sulfoxides³⁾ involving either supported reagents⁴⁾ or electrochemical methods,⁵⁾ the present method is a useful alternative to the conventional methods due to the following features and advantages. (1) The reaction is highly selective and sulfides essentially free from sulfone are obtained in high yields. (2) The procedure is quite simple and the product can be isolated by filtration followed by simple distillation. (3) The resin beads are reusable. (4) Only the electricity and water are consumed during the reaction.

The mechanism of this reaction will be discussed elsewhere.

Experimental

General. A Trio Model PR-653 regulated DC power supply or Kikusui Model PAB-32-0.5 regulated DC power supply was used as a source of electric current. ¹H NMR spectra were recorded on a Varian T-60A spectrometer in carbon tetrachloride using tetramethylsilane as an internal standard. IR spectra were recorded on a Hitachi Model 215 grating spectrophotometer. GLC analysis were performed on

a Shimadzu GC-4B or GC-4C gas chromatograph.

Materials. Crosslinked poly(4-vinylpyridine) hydrobromide (PVP·HBr) and crosslinked poly(4-vinylpyridine) hydrochloride (PVP·HCl) were prepared as reported previously.¹⁾ Other chemicals were used as obtained commercially.

Electrochemical Oxidation of Sulfides. The reactions were carried out in an undivided cell equipped with two platinum electrodes (10×10×0.5 mm³) parallel to each other with about 10 mm of space between them. A sulfide (20 mmol) and PVP·HBr (3.0 g, wet) were allowed to react in 3.0 ml of acetonitrile with a constant electric current (50 mA) at 30 °C under slow stirring. The crude reaction mixture was analyzed by GLC. The mixture was filtered and the filtrate was dried over Na₂SO₄. After evaporation of the solvent, bulb-to-bulb distillation of the residue yielded the products, which were identified by comparison of their IR and ¹H NMR spectra with those of authentic materials.

We thank Koei Chemical Co., Ltd, for gifts of 4-vinylpyridine and divinylbenzene. We are also grateful to the Ministry of Education, Science and Culture for a Grant-in-Aid for Scientific Research No. 56750598 for partial support of this work.

References

- 1) J. Yoshida, R. Nakai, and N. Kawabata, *J. Org. Chem.*, **45**, 5269 (1980).
- 2) Indirect electrochemical oxidation reactions using the bromide ion as mediator have been reported. For example, T. Shono, Y. Matsumura, S. Yamane, and S. Kashimura, *Chem. Lett.*, **1982**, 565; S. Torii, K. Uneyama, H. Tanaka, T. Yamanaka, T. Yasuda, M. Ono, and Y. Kohmoto, *J. Org. Chem.*, **46**, 3312 (1981); S. Torii, K. Uneyama, M. Ono, H. Tazawa, and S. Matsunami, *Tetrahedron Lett.*, **1979**, 4661.
- 3) S. R. Sandler and W. Karo, "Organic Functional Group Preparation," Academic Press (1968), Chap. 19.
- 4) K. T. Liu and Y.-C. Tong, *J. Org. Chem.*, **43**, 2717 (1978).
- 5) P. T. Cottrell and C. K. Mann, *J. Electrochem. Soc.*, **116**, 1499 (1969); K. Uneyama and S. Torii, *Tetrahedron Lett.*, **1971**, 329; B. E. Firth and L. L. Miller, *J. Am. Chem. Soc.*, **98**, 8272 (1976).