Polarographic Estimation of Benzothiophene-1-dioxide and Related Compounds

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The work was undertaken to investigate the application of the polarograph to the determination of benzothiophene and certain of its derivatives. Benzothiophene-1-dioxide, 2,3-dichloro-, 3-chloro-, and 3-bromobenzothiophene-1-dioxide were found to be polarographically reducible in an ammoniacal chloride solution. Benzothiophene, 3bromo- and 2,3-dihydrobenzothiophene, and 2,3dihydrobenzothiophene-1-dioxide were not reduced under the same conditions. It is concluded that for the reduction to take place, the benzothiophene derivative must contain a double bond in the 2,3 position and a dioxide group in the 1 position. A basic procedure for the quantitative determination of benzothiophene-1-dioxide and certain halogen derivatives is a significant addition to the field of organic sulfur chemistry.

INTEREST in certain derivatives of benzothiophene led to a study of their polarographic behavior. The literature relating to this field is rather limited. Wawzonek (5) points out that the disulfide linkage is apparently the only sulfur grouping which is reduced at the dropping mercury electrode. Kolthoff and Lingane (4) described the catalytic hydrogen wave produced by certain compounds containing sulfhydryl groups in ammonium chloride-ammonia and in ammoniacal cobalt solutions.

EXPERIMENTAL

A Sargent polarograph, Model XII, having a galvanometer sensitivity of 0.0037μ a. per mm., was used for this investigation. The cell(3) consisted of a stationary pool of mercury serving as the anode and a dropping mercury cathode with the following characteristics:

T (drop time). 3.8 seconds per drop

Mass of mercury. 1.75 mg. per second. $m^{2/3} \times T^{1/6}$. 1.81

Sample solutions were maintained at 25 ° C. in a suitable water

Table I. Diffusion Currents of Benzothiophene-1-dioxide and Halogen Derivatives

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Compound	Conen., Mg./100 Ml.	Step Height, Mm.	μа.	µa.∕ Millimole	μa./ Milliatom Halogen	Half-Wave Potential Volts
Benzothiophene-1- dioxide ^a	$\frac{1}{2}$ 5	$51.5 \\ 103.5 \\ 256$	$\begin{array}{c} 0.191 \\ 0.381 \\ 0.947 \end{array}$	$\begin{array}{c} 31.7\\ 31.6\\ 31.4 \end{array}$	• • • • • • • •	-1.2
3-Bromobenzothio- phene-1-dioxide ^b	$1 \\ 2 \\ 5$	${}^{60.5}_{122}_{295}$	$\begin{array}{c} 0.224 \\ 0.451 \\ 1.091 \end{array}$	$54.8 \\ 55.3 \\ 53.4$	$23.2 \\ 23.7 \\ 21.8$	-0.97, -1.1
2-Bromobenzothio- phene-1-dioxide ^c	$1 \\ 2 \\ 5$		$\begin{array}{c} 0.222 \\ 0.451 \\ 1.128 \end{array}$	$54.4 \\ 55.4 \\ 55.3$	$22.8 \\ 23.8 \\ 23.7$	-0.95, -1.2
2,3-Dichlorobenzothio- phene-1-dioxide ^d	$1 \\ 2 \\ 5$	$96 \\ 186 \\ 478$	$\begin{array}{c} 0.355 \\ 0.688 \\ 1.769 \end{array}$	83.5 80.9 83.2	$25.9 \\ 24.6 \\ 25.8$	-0.92, -1.2
3-Chlorobenzothio- phene-1-dioxide ^e	$1 \\ 2 \\ 5$	$\begin{array}{r} 75.9 \\ 148 \\ 342.4 \end{array}$	$\begin{array}{c} 0.281 \\ 0.548 \\ 1.267 \end{array}$	$\begin{array}{c} 56.4\\54.9\\50.8\end{array}$	$24.8 \\ 23.3 \\ 19.2$	~ 0.92, − 1.2
 ^a Melting point 142-143° C. Prepared by H₂O₂ oxidation of benzothiophene. ^b Melting point 182-184° C. Prepared according to Bordwell and Albisetti (1). ^c Melting point 150-151° C. Prepared according to Bordwell et al. (2). ^d Melting point 158-159° C. Prepared by H₂O₂ oxidation of 2.3-dichlorobenzothiophene. ^e Melting point 163-164° C. Prepared by H₂O₂ oxidation of 3-chlorobenzothiophene. 						

bath and were purged with nitrogen for 5 minutes before polarograms were taken.

At the beginning of this investigation, reduction of benzothiophene-1-dioxide in 0.1 N solutions of the usual electrolytes such as potassium, ammonium, and lithium chlorides and hydrochloric acid in 1 to 1 alcohol-water solutions gave poorly defined waves over the range of 0.0 to -2.0 volts. Reduction was effected by using 1 N ammonium chloride in the same solvent. Addition of ammonium hydroxide to produce a pH of 8.5 did not change the reduction wave. Addition of hydrochloric acid to give a pH of 1.5 resulted in a hydrogen wave. Benzothiophene-1-dioxide and its halogen derivatives were also reduced in an ammoniacal cobalt solution. The reduction current was proportional to the concentration of the sulfones after subtraction of the current due to the presence of cobalt. However, for the present work cobalt was not necessary.

DISCUSSION

Data in Table I show that the diffusion current obtained is proportional to the concentration of benzothiophene-1-dioxide. The half-wave potential is -1.2 volts, and the diffusion current is 31.6 μ a. per millimole. To determine the interference of certain related benzothiophenes, solutions of benzothiophene-1-dioxide were prepared and one of the following compounds was added: benzothiophene, 3-bromobenzothiophene, 2,3-dichlorobenzothiophene, 2,3-dihydrobenzothiophene, 2,3-dihydrobenzothiophene, 2,3-dihydrobenzothiophene, 1-dioxide. None of these affected the reduction wave. A diffusion current of 36 μ a, per millimole was obtained with 2,3-dibromo-2,3-dihydrobenzothiophene-1-dioxide. This abnormal reduction current may be attributed to the partial splitting off of hydrobromic acid to form some monobromobenzothiophene-1-dioxide under the conditions of the experiment.

Table I also gives the results obtained on several benzothiophene-1-dioxides containing halogens substituted in the 2 and 3 positions. For these compounds the reduction wave was also proportional to the halogen present in the molecule. In all cases the two waves which formed were rather indistinct, owing to the small differences in half-wave potentials. However, in the reduc-

> tion wave of 2,3-dichlorobenzothiophene-1-dioxide it appeared that the reduction of the vinyl sulfone portion of the molecule was affected at the lower half-wave potential (-0.92 volt).

CONCLUSION

From the data obtained it is concluded that if the reduction is to take place the benzothiophene derivative must contain a double bond in the 2,3 position and a dioxide group at the 1 position. Substituted chlorine and bromine in the 2 and 3 positions are also reduced polarographically.

LITERATURE CITED

- Bordwell, F. G., and Albisetti, C. J., Jr., J. Am. Chem. Soc., 70, 1559 (1948).
- (2) Bordwell, F. G., et al., Ibid., 71, 1702 (1949).
- (3) Kolthoff, I. M., and Lingane, J. J., "Polarography," p. 63, New York, Interscience Publishers, 1941.
- (4) Ibid., p. 405.
- (5) Wawzonek, S., ANAL. CHEM., 21, 61 (1949).

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