−30 to −50°. Distillation was continued with heating until no further separation of halide was observed on addition of a saturated solution of sodium chloride. Crude vinyl iodide was thus separated, washed with dilute sodium bisulfite solution, with water and finally dried over calcium chloride. On redistillation practically all the product passed over at a temperature of 56–56.5°. Approximately 50 g. was obtained. The refractivity was determined. Owing to the ease of oxidation of vinyl iodide the observations were made in an atmosphere of nitrogen.

SPECIFIC GRAVITY 2.037 (20°)

Line	Index of refraction	Molecular refraction (found)	Molecular refraction (calcd.)
Hydrogen (α)	1.53232	23.365	23.546
Sodium (D)	1.53845	23.651	23.769
Hydrogen (β)	1.55186	24.153	24.209
Hydrogen (γ)	1.56468	24.495	24.706

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The Mechanism of the Reduction of Sulfonyl Halides by Phosphorus Tribromide

BY A. H. KOHLHASE[1]

In a recent paper, Hunter and Sorenson[2] have stated that "previous work[3] has shown that sulfonyl chlorides are not reduced by phosphorus tribromide." This is in error as Kohlhase showed (Table I and Experiment XI) that 3-nitro-6-methylbenzenesulfonyl chloride was reduced readily and in good yield to the corresponding disulfide. It is true that sulfonyl chlorides were reduced far less *readily* than the corresponding bromides.

Kohlhase had concluded that the thiols formed in two instances of the reduction of sulfonyl derivatives by phosphorus tribromide, resulted as follows

$$\mathrm{RSSR} + \mathrm{PBr_3} \rightleftharpoons \mathrm{(RS)_2{\cdot}PBr_3}$$
$$\mathrm{(RS)_2{\cdot}PBr_3} + 4\mathrm{H_2O} \longrightarrow 2\mathrm{RSH} + 3\mathrm{HBr} + \mathrm{H_3PO_4}$$

Hunter and Sorenson concluded that the mechanism is

$$\mathrm{RSO_2Br} \xrightarrow{\mathrm{PBr_3}} \mathrm{RSBr} \xrightarrow{\mathrm{PBr_3}} \mathrm{RSPBr_4} \xrightarrow{4\mathrm{H_2O}} 2\mathrm{RSH} + 4\mathrm{HBr} + 2\mathrm{H_3PO_4}$$

This interpretation seems rather convincing but Kohlhase[3] showed that phenyl 3,5-dinitrobenzenethiosulfonate, treated with phosphorus tribromide and then with ether and water, gave a very good yield of 3,5-di-

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(1) Present address, Whipple, Arizona.

(2) Hunter and Sorenson, THIS JOURNAL, **54**, 3368 (1932).

(3) Kohlhase, *ibid.*, **54**, 2441 (1932).

nitrothiophenol. Here the intermediate formation of a sulfur bromide is hardly possible and the mechanism originally proposed by Kohlhase seems the only one available. It is quite probable that in these reductions of all RSO_2X derivatives by phosphorus tribromide, *both* mechanisms may be operative, the relative speeds depending on conditions and on the nature of R and X, although the mechanism of Hunter and Sorenson is undoubtedly the chief one in *most* cases where a thiol is produced.

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Notes on the Thompson–Oakdale Method for the Determination of Halogen in Organic Compounds

BY J. J. THOMPSON AND U. O. OAKDALE

The Thompson–Oakdale method[1] for the determination of halogen has been used with excellent results in hundreds of instances in our laboratories. However, the fact is not always recognized that the alkaline solution of the halide contains a considerable amount of sodium sulfite and consequently erroneous results may be obtained in the gravimetric estimation of the halogen due to the fact that the precipitated silver halide is apt to be contaminated, possibly with silver sulfide formed by decomposition of silver sulfite. This difficulty may be obviated in the following manner. The alkaline solution to which sodium arsenite has been added in accordance with the original directions is poured into a beaker, cooled thoroughly and after the addition of about 5 cc. of superoxol or perhydrol, to oxidize the alkaline sulfite to sulfate, the mixture is stirred and boiled for a few minutes. The solution is then cooled, acidified with nitric acid and the halide precipitated in the usual manner.

In view of our observations on the use of this method by students it seems necessary to emphasize the fact that *all* of the halogen, especially in the case of iodine, cannot be driven through the condenser into the alkaline solution unless the mixture in the Kjeldahl flask is boiled in such a manner that a continuous stream of steam passes through the apparatus for a short time.

The potassium persulfate used must always be tested for perchlorate since many commercial brands of persulfate contain this impurity. Potassium persulfate, free from perchlorate, is now available commercially (Mallinckrodt Chemical Works).

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(1) Thompson and Oakdale, THIS JOURNAL, **52**, 1195 (1930).