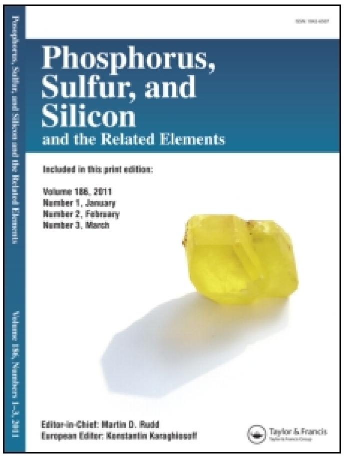

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SULFENAMIDES AND SULFINAMIDES XI.† OXIDATION OF IODIDE ION BY AN ARYL SULFINAMIDE

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Oxidation of hydriodic acid by an aryl sulfinamide produced iodine in excess of the stoichiometric amount given by sulfoxides. The excess is explained by a secondary reaction with sulfenamide, the initial product, but is lessened by tertiary reactions including the formation of iodoaniline.

Key words: Sulfenamide, sulfinamide, disulfide, iodide, oxidation, thiol.

INTRODUCTION

The oxidizing power of the sulfinyl group as in dimethyl sulfoxide has been applied to a wide variety of substrates.[1] As a result it has been suggested that many oxidations proceed through an intermediate dimethylalkoxysulfonium salt formed by one or other of two routes depending on the structure of the substrate (Scheme 1).

The first involves direct displacement of a leaving group X (X = Cl, Br, I), with dimethyl sulfoxide as a nucleophile.[2–4] This principle has been used for the oxidation of α-halogeno ketones[5] and α-halogeno esters,[6] generally at room temperature.

$$\text{p-BrC}_6\text{H}_4\text{COCH}_2\text{Br} \rightarrow \text{p-BrC}_6\text{H}_4\text{COCHO}$$

$$\text{BrCH}_2\text{COOC}_2\text{H}_5 \rightarrow \text{OCHCOOC}_2\text{H}_5$$

Longer chain alkyl iodides are readily converted to aldehydes at high temperature (~140–150°C).[7] Less reactive halides may be converted to tosylates before reacting with dimethyl sulfoxides[8] but these and certain benzyl halides[8,9] are also believed to react according to pathway **I** above (Scheme 1).

Pathway **II** (Scheme 1) provides a basis for discussing iodide oxidation. In acidic medium the oxidation, despite the simplicity of the summarizing expression, has provided considerable discussion on mechanism and kinetics.[10,11]

$$\text{R}_2\text{SO} + 2\text{I}^- + 2\text{H}^+ \rightarrow \text{R}_2\text{S} + \text{I}_2 + \text{H}_2\text{O}$$

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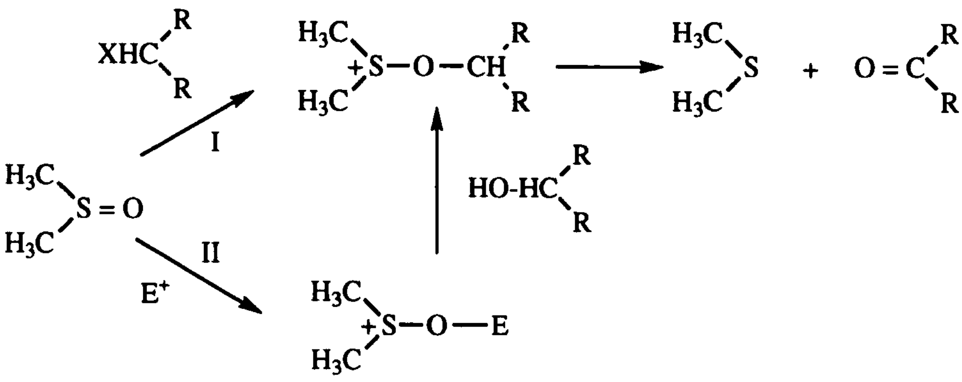
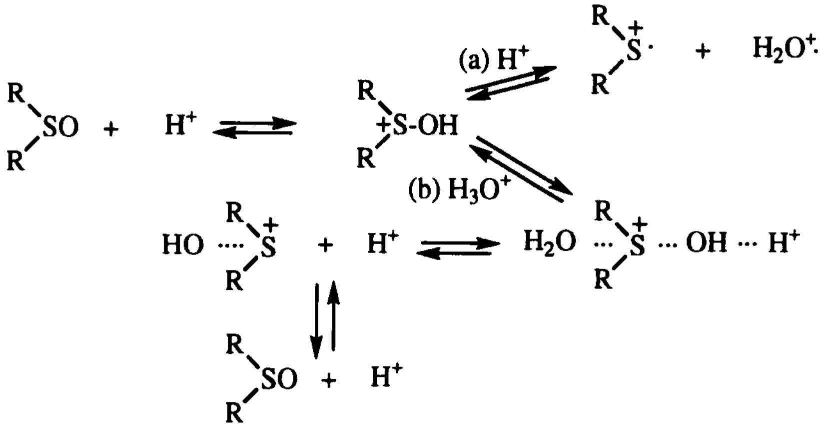
†Visiting scholar from Meiji University, Japan.

‡Part X, *Phosph., Sulfur and Silicon* (in submission).



Scheme 1

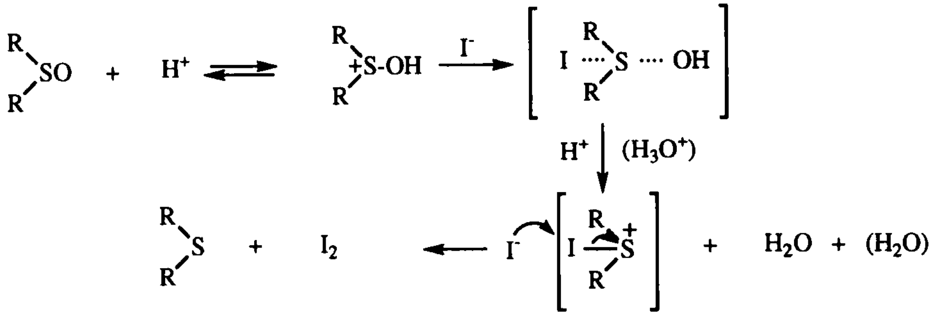


Scheme 2

The oxidation has generally been reported at first order in sulfoxide and iodide,[12] although a zero order in iodide has been reported in special cases as with sulfinyl carboxylic acids.[13] The reaction is catalyzed by acid with a changing order of dependence according to the dilution of the medium.[14]

In strong acid (>80% strength) processes may favor a type (a) S_N^1 course (Scheme 2) but in the more usual dilute acid conditions reaction occurs by type (b) S_N^2 displacement at the sulfur atom[15] (Scheme 2). It may be noted that oxygen exchange and racemization of optically active sulfoxides then occur at the same rate. These reactions are reversible but with iodide now performing the nucleophilic role the reaction becomes irreversible (Scheme 3).

It is interesting to note the equivalent reaction in acetic acid of the sulfinyl group of thiosulfinates where the group, linked to another sulfur atom, is used for determinations of purity and estimation. Thus the reaction proceeds without apparent interference from the second sulfur atom.[16] In continuing studies of reactions featuring the S—N bond, the environment of the sulfinyl group has been transferred to that of an acid amide where, as with the oxidation of thiols,[17] the possibility of different courses of reaction appears.



Scheme 3

RESULTS AND DISCUSSION

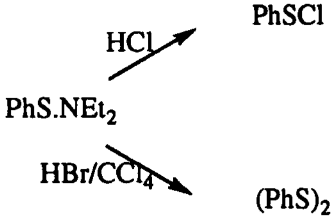
A superficial analogy of the sulfinamide/iodide reaction with the sulfinamide/thiol reaction was suggested by the rapid appearance of iodine, some aniline and a quantitative recovery of diphenyl disulfide from a larger scale experiment. However, the analogy was brought into question by determinations of the amount of iodine found, up to 130% of that indicated by the simple stoichiometric expression (1) based on reduction to sulfenamide by a process similar to that discussed for the reduction of sulfoxide ion.

$$C_6H_5SO \cdot NHC_6H_5 + 2I^- + 2H^+ \rightarrow C_6H_5S \cdot NHC_6H_5 + I_2 + H_2O \quad (1)$$

In this respect results are unusual since most experiments which give further reactions lead to lower yields. As a starting point in the accountability it may be considered that subsequent reactions begin with fission of the sulfenamide giving a sulfenyl iodide in a reaction representing the reverse of that occurring in sulfenamide synthesis.

$$C_6H_5S \cdot NHC_6H_5 + HI \rightarrow [C_6H_5SI] + H_2NC_6H_5 \quad (2)$$

Fission of N,N-diethylbenzenesulfenamide with hydrochloric or hydrobromic acids has shown that halogen acid cleavage of sulfenamides may not always produce the sulfenyl halide.[18] In the event of initial derivative instability the product may be disulfide.[19]



Thus it could reasonably be expected that a sulfenyl iodide would show an even greater tendency to yield disulfide, either by decomposition (a) or by further reaction with hydrogen iodide (b) (Scheme 4). Reaction (b) is similar to that used for the estimation of sulfenyl halides.[20,21]

The fact that the equilibrium RSSR + X_2 = 2RSX lies largely to the left when X = I has been used to account for the recording of comparatively few stable sulfenyl iodides. Both of the above processes would lead to formation of iodine to the extent of 150% of that indicated by the base reaction (1), but this is subject to reduction to the extent a tertiary reaction with aniline occurs. Theoretically the decomposition of the sulfenamide (reaction (2)) would release one molecule of aniline which would allow for reaction with at least one molecule of iodine in forming a mono-iodo derivative.

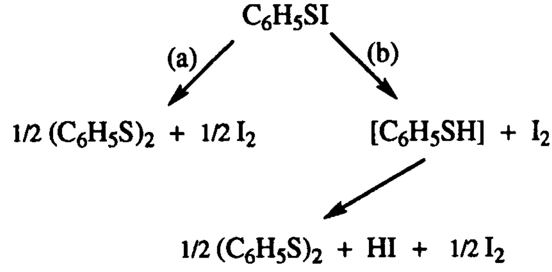
$$C_6H_5NH_2 + I_2 \rightarrow IC_6H_5NH_2 + HI$$

Analysis of the product mixture by TLC and GC/MS showed both free aniline and its 4-iodo derivative, so that recoveries of iodine of 120–130% suggest that this reaction occurred rather slowly, to a maximum of 30% in the time allowed. Results show that formation of iodine which is quantitative in the case of the thiosulfinates, is not so in the case of the sulfinamides for two counterpoised reasons—the generation of excess iodine with sulfenamide some of which is then removed by reaction with the amine.

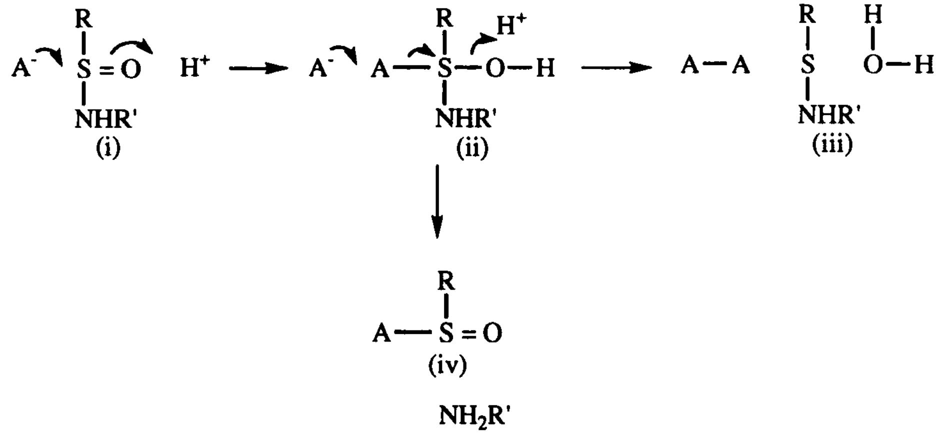
A minor product of the reaction was phenyl benzenethiosulfonate whose presence may be accounted for as follows. Reaction of the first-formed sulfenamide with a second molecule of hydriodic acid produces a second molecule of iodine and a molecule of thiophenol (reaction (2) followed by reaction (b) Scheme 4). The thiophenol may be oxidized by the iodine to disulfide or, alternatively, some of it may react with sulfinamide to form the thiosulfinate, disproportionation of which would yield thiosulfonate.

It is interesting to compare the reactions of sulfinamides with hydrogen iodide on the one hand and a thiol on the other. In Scheme 5, the ion A^- may be either iodide or thiolate (RS^-).

In both cases the first step in the reaction of HA with the sulfinamide (i) to form intermediate (ii). In the iodide reaction, step 2 involves the relay of electrons from a second molecule of iodide through sulfur to oxygen liberating iodine (A—A), a sulfenamide (iii) and water. If the thiol reaction proceeded in the same manner, the products would be a disulfide (A—A), sulfenamide (iii) and water. However in the thiol reaction, intermediate (ii) evidently decomposes to liberate the thiosulfinate (iv) and an amine ($R'NH_2$). The difference between the two pathways can probably be explained in terms of the strength of the S—A bond. When A is iodine, the S—A bond of (ii) is much weaker than its S—N bond for reasons



Scheme 4



Scheme 5

discussed above. Thus decomposition of (ii) to (iv) is less likely since it would involve breakage of the stronger rather than the weaker bond and, in any case, (iv) would be expected to react immediately with $R'NH_2$ to reform the more stable (i). However, when A is a thiol, the S—A bond of (ii) is stronger than its S—N bond and consequently the molecule decomposes to yield (iv).

EXPERIMENTAL

Sulfenamides, sulfinamides and other reference materials were prepared by standard methods as previously described in this series.

Thin layer chromatography was performed using three systems; (i) on silica gel plates (0.5 mm) with benzene/ethyl acetate (10:1) or (ii) benzene as developing solvent and (iii) on kieselguhr G plates impregnated using a solution of liquid paraffin (3% v/v) in acetone with methanol/water (7:3) as developing solvent. Gas chromatography-mass spectrometry (GC/MS) was performed on a Hewlett Packard 5890 series 2 gas chromatograph interfaced with a Hewlett Packard 5971A mass selective detector (MSD) using a BP-1(12m × 0.22 mm; SGE) column.

Oxidation of iodide. The procedure was that previously described for the estimation of thiosulfinates.[16] To the sulfinamide (40–50 mg) in oxygen-free acetic acid under nitrogen in a small flask provided with side arm and magnetic stirrer, was added a saturated aqueous solution of potassium iodide (2 mL). After 2 min of stirring, liberated iodine was titrated slowly with 0.02M sodium thiosulfate to a starch end point. Results are given in Table I.

Products of reaction.

(a) Diphenyl disulfide. To N-phenylbenzenesulfinamide (1.304 g) in acetic acid (200 mL) was added a saturated solution of potassium iodide (40 mL). After 10 min of stirring, water (800 mL) was added and the resulting precipitate of diphenyl disulfide (0.600 g, 92%) recovered by filtration. The recrystallized material had mp and mixed mp 58°C with IR spectrum and R_f values, using systems (i) and (iii), identical with those of diphenyl disulfide.

(b) 4-Iodoaniline appeared to be a major by-product with the same R_f values (0.51 in benzene/ethyl acetate (10:1) and 0.31 in benzene) and rapid darkening of spots on chromatograms as reference material obtained from an iodine/aniline reaction. Because of the instability of this compound it had partly decomposed before a GC/MS run on it could be made. Nonetheless a significant amount of 4-iodoaniline was noted together with other unidentified compounds. MS (ei) m/z (rel. intensity) 219$[M^+]$ (100), 127 (4), 92 (29), 65 (19).

TABLE I

Reaction of N-phenyl benzenesulfinamide with iodide in acetic acid

Sample (g)	0.02M $Na_2S_2O_3$ (mL)	Iodine*
0.0442	24.7	121
0.0438	25.2	125
0.0406	24.3	130

* % of theory for conversion to sulfenamide

(c) Phenyl benzenethiosulfonate was isolated from TLC plates with an R_f of 0.68 (solvent benzene) and mp 37–38°C (Lit[22]. mp 38°C). MS (ei) m/z (rel. intensity) 250 [M^+] (34), 218 (1), 141 (39), 125 (100), 109 (37), 77 (66).

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