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Derivatives of 1,2-Dithiole-3-thione. XI. A Kinetic Study of the Reduction of *N*-Phenylsulfonyl Thione *S*-Imide with Halide

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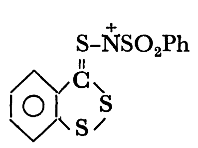
Synopsis. *N*-Phenylsulfonyl thione *S*-imide(I) was reduced with tetra-*n*-butylammonium bromide and iodide in the presence of trichloroacetic acid to yield benzotrithione and the sulfonamide in good yields. The kinetics of the reaction was performed, and the mechanism was discussed in detailed.

Earlier we reported[1)] the isolation and characterization of the thione *S*-imide(I) formed in the reaction of chloramine-B with 1,2-benzodithiole-3-thione (benzotrithione).



(I)

Our primary interest in this new type of the compound was to elucidate the mechanism of its formation. Previously,[2)] the reaction of diphenyl sulfide with chloramine-T was found to be acid-catalyzed and to take place through an initial chlorination of the sulfur atom to give the chlorosulfonium ion, followed by nucleophilic displacement with the sulfonamide anion; the rate-limiting step is the former rather than the latter step.

Quite contrary to the rate of common sulfilimide formation, the thione *S*-imide formation did not allow us to determine its rate because the rate of the reaction was too fast for us to employ the usual techniques even at a neutral pH. The object of the present study was to examine the reduction of the thione *S*-imide with halide, since although the rate of the formation could not be followed by our usual means, as has been stated above, an examination of the reduction should clarify the mode of its reverse reaction, *i.e.* the formation, according to the microscopic reversibility principle.

Results and Discussion

When the thiocarbonyl *S*-imide(I) was treated with an equimolar amount of tetra-*n*-butylammonium bromide (Br^-) or iodide in CH_3CN containing a five-fold excess of trichloroacetic acid (H^+) at room temperature for 20 min, benzotrithione and benzenesulfonamide were both obtained in excellent yields.

The reaction was catalyzed essentially by acids with pH values of a moderate strength. In fact, a weak acid such as acetic acid with a pH of 4.76 did not catalyzed the reduction, not even in a neat acetic acid solution.

The kinetic study of the reaction of *S*-imide with bromide was carried out in some detail by adding a large excess of acid and by monitoring the increase in the absorbance due to the reduced trithione appearing at 445 nm. At high acid concentrations, as the UV spectra indicate, all the *S*-imide has been protonated on the nitrogen atom; that is, the protonated *S*-imide is the only predominant species at the initial stage of the reaction. Indeed, there is an isosbestic point at 443 nm between the benzotrithione produced and what appears to the protonated *S*-imide (Fig. 1). The data for the substituent effect on the rate are collected in Table 1, where k_0 is the observed first-order-rate constant of the reaction, which follows simple first-order kinetics.

First, we attempted to determine the kinetic order with regard to both the acid and bromide concentrations. At a large excess of acid concentrations relative to the *S*-imide, additional protic acid did not play any important role in accelerating the rate, as is shown in Fig. 2. Under these reaction conditions, kinetic experiments at different initial concentrations of bromide salt were performed and showed that the rate constants(k_0) thus determined did not follow the usual first-order kinetics with regard to the bromide concentrations, but gave a correlation represented by a down-concave curvature, as is shown in Fig. 3.

In the initial range of the plot the rate appears to obey first-order kinetics, while at the higher bromide concentrations the rate appears to be essentially independent of the bromide concentration. It thus seems clear that the reaction is indeed consistent with

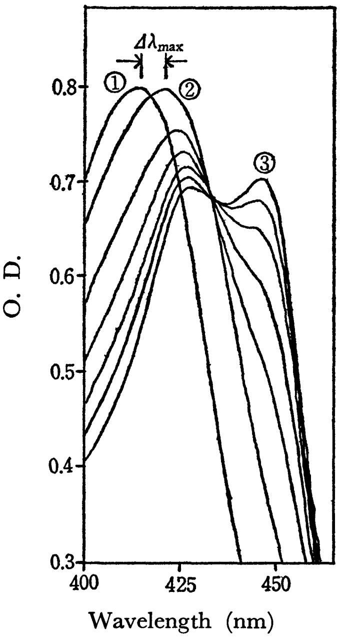


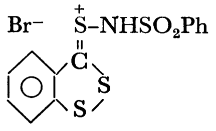
Fig. 1. Reduction of I with Br^- in the presence of Cl_3CCOOH.
①: (I) + H^+, ②: (I)+H^++Br^-, ③: benzotrithione

Table 1. Kinetic data for the reduction of various substituted thiocarbonyl *S*-imide with Br^- in the presence of Cl_3CCOOH

Substituent(X)	CH_3	H	Br	*m*-NO_2
$k_0\times10^5\ s^{-1}$	5.78	7.34	13.4	30.7

$[Br^-]=8.01\times10^{-4}$ M, $[H^+]=1.21\times10^{-1}$ M, $[I]=1.00\times10^{-4}$ M, at 25.25 °C.

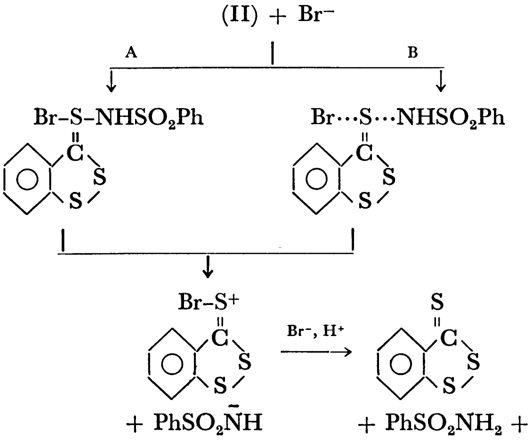
step-by-step processes involving the buld-up of at least one Br^--containing intermediate, which we assumed to be an intimate ion-pair(II).



ion-pair (II)

In Fig. 3 a plot of the change of the UV maxima against varying bromide concentrations is also shown. An inspection of Fig. 3 reveals that the change in the absorption maximum by varying the bromide concentration gives a good parallelism with the change in the rates. This observation can best be accounted for by a specific solute-solute interaction between the protonated *S*-imide and Br^-; that is, the reduction takes place *via* the formation of quite a stable intimate ion-pair intermediate(II).

The Hammett plot of the data(Table 1) gives the best linear correlation with the σ_p values for the para-substituted *S*-imide. The direction of the substituent effect is shown by the large, positive value of $\rho=0.9$ indicating that, in the rate-determining step, the S-NSO_2 bond cleavage apparently takes place. The two reaction mechanisms, A and B, fit the experimental data thus obtained.



Both the activation energy and entropy, 13 kcal/mol and −25 eu respectively, at $[Br^-]=8.01\times10^{-4}$ M and $[H^+]=1.21\times10^{-1}$ M are well consistent with these mechanisms. The first one (A) involves the addition-elimination of the nucleophilic Br^- ion on the sulfur atom, followed by the rate-determining N–S bond cleavage, leading to a bromonium salt and eventually giving the reduced trithione. Meanwhile, the (B) mechanism resembles that outlined for a usual S_N2 reaction on a carbon atom; this process requires a one-step displacement of the leaving sulfonamide anion by the bromide anion.

Based on only the limited data available it is difficult to decide whether or not this reduction involves an discrete addition intermediate. However, a more plausible mechanism would be the process like A which includes the intervention of an addition complex in which the entering and leaving groups are bonded to the central sulfur atom. Such a hypervalent intermediate has been documented in other substitution reactions³⁾ and, in some cases, isolated.⁴⁾ In fact, quite a structurally similar planar compound has recently been synthesized.⁵⁾

Finally, it should be emphasized that the Br^--reduction itself is the reverse of the formation of the *S*-imide from the trithione and chloramine-B. From a consideration of the microscopic reversibility, it can be said that the *S*-imide is probably produced not by the mechanism involving the initial halogenation as the rate-controlling step, but rather, by the rate-determining attack of the sulfonamide anion on the halogenated trithione in sharp contrast to the mechanism of the formation of the sulfilimide where the halogenation is the rate-determing step.²⁾

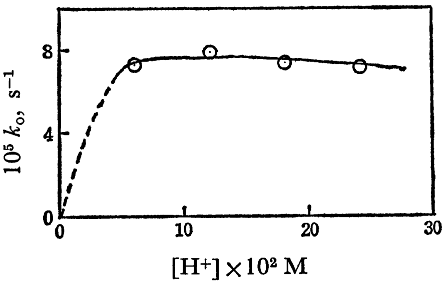


Fig. 2. Plot of the rate constant against acid concentration at 25 °C in CH_3CN. $[Br^-]=8.01\times10^{-4}$ M, $[I]=1.00\times10^{-4}$ M.

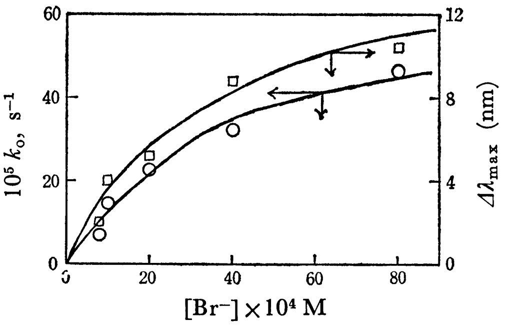


Fig. 3. Plots of the rate constant and $\Delta\lambda_{max}$ against Br^- concentration in the presence of a large excess of acid at 25 °C in CH_3CN. $[CCl_3COOH]=1.21\times10^{-1}$ M, $[I]=1.00\times10^{-1}$ M.

Experimental

Kinetics. The rates were determined spectrophotometrically by employing the usual techniques.

Products. The *S*-imide (339 mg) was treated with an equimolar amount of tetra-*n*-butylammonium bromide and a five-fold excess of Cl_3CCOOH in CH_3CN at room temperature. After 20 min, the solvent was evaporated *in vacuo* and the residue was treated with a dilute $Na_2S_2O_3$ solution. Extraction with ether, the evaporation of the ether, and the chromatographic separation of the extract on silica plates, using benzene as the eluent, gave benzotrithione (85.9%) as well as benzenesulfonamide (91.1%)

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