

AN ABSTRACT OF THE THESIS OF

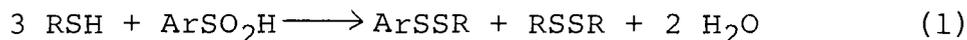
Gary Ronald Bray for the Master of Science in
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Organic Chemistry
(Major)

Date thesis is presented May 29, 1963 - 

Title The Reactions of p-Toluenesulfinic Acid with
Mercaptans and Secondary Alkyl Sulfides

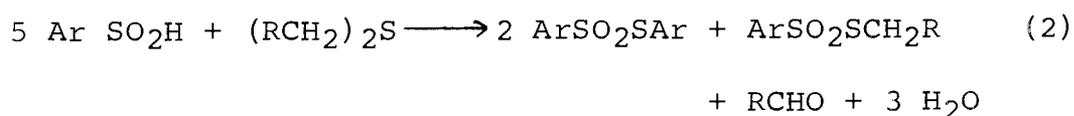
Isopropyl, butyl or benzyl mercaptan all react very rapidly with p-toluenesulfinic acid in acetic acid-0.56 M water-0.6 M sulfuric acid solution at 70°. If the mercaptan is added rapidly as a concentrated solution three moles of mercaptan react per mole of sulfinic acid present. The reaction products in each case are two disulfides, the first being the symmetrical derived from the mercaptan used, the second, the unsymmetrical p-tolyl alkyl disulfide. About equimolar amounts of the two disulfides were isolated in each case. Under the reaction conditions employed the mercaptan-sulfinic acid reaction clearly has the stoichiometry



These results are compared with those obtained under other conditions both in this laboratory and elsewhere, and

some tentative conclusions about the details of the mechanism of the mercaptan-sulfinic acid reaction are outlined.

Recently Kice and Bowers discovered a new reaction of sulfinic acids. This was their reaction with primary alkyl sulfides. For p-toluenesulfinic acid and a primary alkyl sulfide this reaction has the stoichiometry shown below,



It was of interest to determine if this unusual cleavage of a sulfide could be extended to sec-alkyl sulfides.

Studies in the present thesis show that both isopropyl and sec-octyl sulfide react about as readily as primary alkyl sulfides with p-toluenesulfinic acid. Acetone and 2-octanone have been identified as products of their respective reactions. The yields of p-tolyl p-toluene-thiolsulfonate obtained in each case are in agreement with the stoichiometry of equation 2, but the expected sec-alkyl p-toluene-thiolsulfonate has so far not been isolated. It is thought that this may well be due to its decomposing during the work-up procedure used. However, further study is needed before any definite conclusion can be drawn on this last point.

THE REACTIONS OF *p*-TOLUENESULFINIC ACID
WITH MERCAPTANS AND SECONDARY
ALKYL SULFIDES

by

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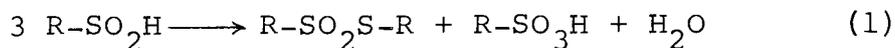
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THE REACTIONS OF p-TOLUENESULFINIC ACID
WITH MERCAPTANS AND SECONDARY
ALKYL SULFIDES

INTRODUCTION

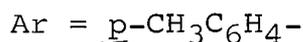
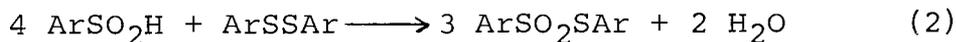
Sulfinic acids have been reported as early as 1860 by Kalle (13) and again in 1861 by Kolbe (13). Several aliphatic and many aromatic sulfinic acids are known. The lower molecular weight sulfinic acids are unstable as the free acid and decompose rapidly, but these same acids are stable as salts. The aromatic sulfinic acids in general are more stable than the aliphatic acids. Some aromatic acids are stable enough to be stored for a considerable period of time as the free acid, provided they are kept in the dark at low temperatures. However, on standing at room temperatures these same acids will undergo disproportionation to sulfonic acid, water, and thiolsulfonate. This reaction was first reported by R. Otto (6) in 1868. The reaction is as follows:



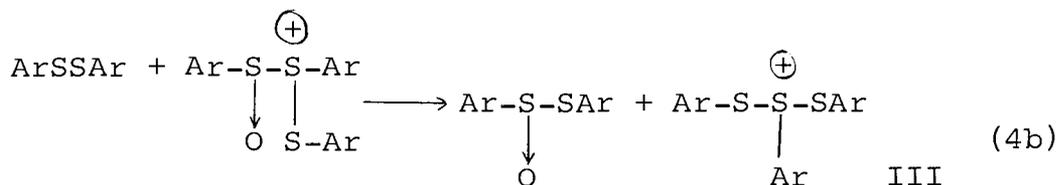
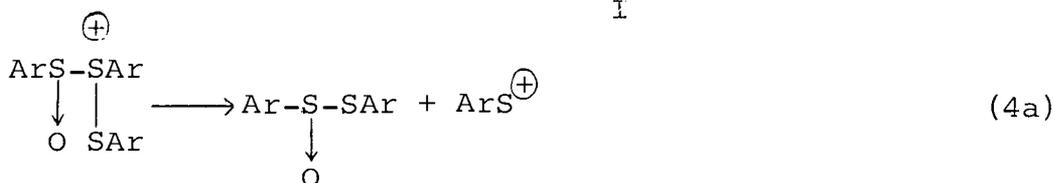
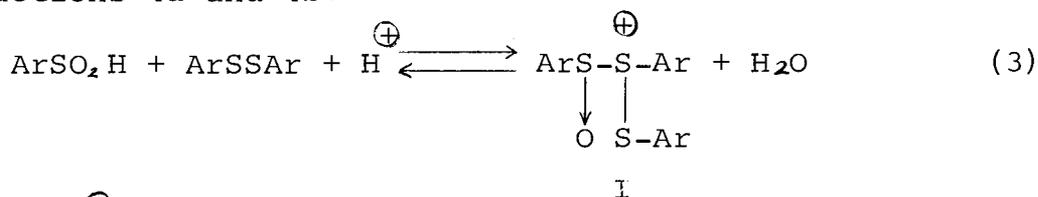
The mechanism of this reaction was first investigated in some detail by Kice and Bowers. In the course of this work Kice and Bowers (6) discovered two previously unreported reactions of sulfinic acids, one a reaction with

disulfides, and the other with primary alkyl sulfides.

The reaction of p-tolyl disulfide with p-toluene-sulfinic acid is as follows:

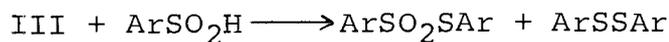
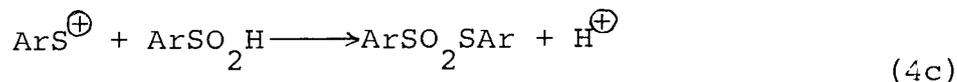


In moist acetic acid containing moderate amounts of added sulfuric acid this reaction predominates strongly over the normal disproportionation of sulfinic acid. The dependence of the rate on the various reaction variables suggests a mechanism in which ion I, formed in the equilibrium shown in equation 3, undergoes rate-determining decomposition by reactions 4a and 4b.



Kice and Bowers suggested that the final products were then formed as follows. Both the sulfenium ion ArS^{\oplus} and ion III were thought to react with sulfinic acid to form

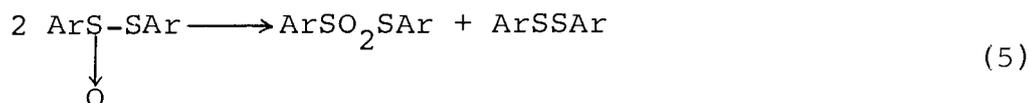
thiolsulfonate.



Thiosulfinates ($\text{ArS}-\text{SAr}$) are known to disproportionate



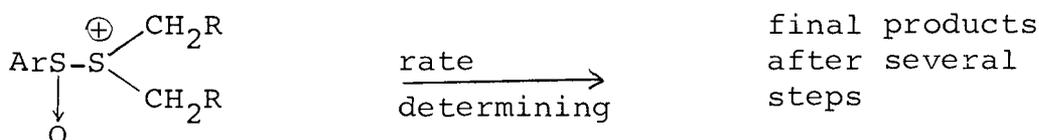
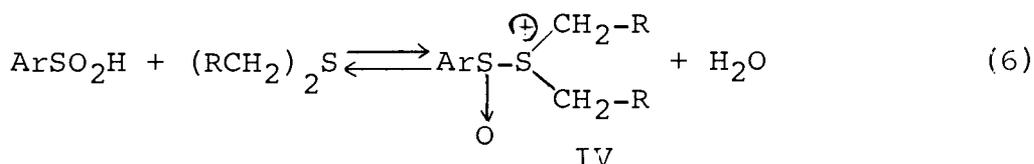
readily to thiolsulfonates and disulfides (14); it was suggested that this occurred here as well.



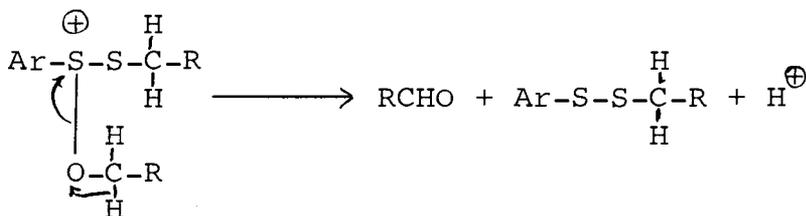
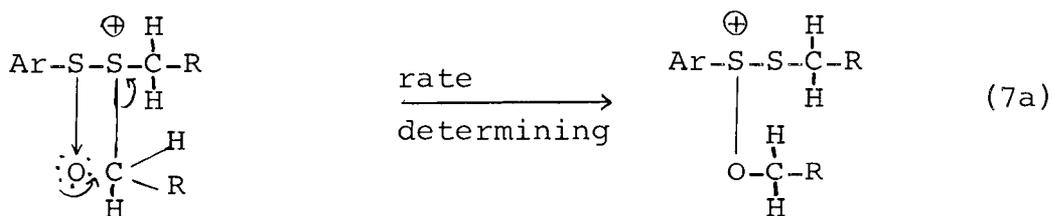
This mechanism would give a total stoichiometry as shown in equation 2, in agreement with the experimental findings.

This raises the possibility that other divalent sulfur compounds ($\text{X}-\text{S}-\text{Y}$) might form ions $\text{ArS}(\text{O})^{\oplus}\text{SXY}$ with sulfinic acid and that these ions could decompose to various products. This was found to be true with primary alkyl sulfides. Again a reaction was found which strongly predominated over the normal disproportionation reaction. This reaction was first order in sulfinic acid and sulfide, and showed the same dependence as the disulfide reaction on water and strong acid concentration. During the course of the reaction one of the alkyl groups of the sulfide was cleaved and oxidized to the corresponding

aldehyde. The kinetic results show that the reaction involves a mechanism in which ion IV is formed in the equilibrium in equation 6 from a sulfide and sulfinic acid and then undergoes rate-determining unimolecular decomposition (eq. 6).



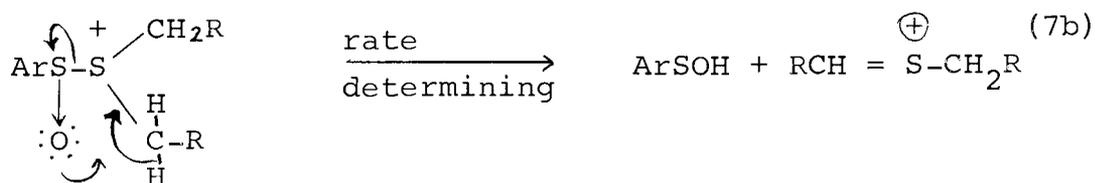
It was originally suggested that this decomposition yielded an aldehyde as shown below.



An alternative path is possible as shown in equation 7b.

To decide between these two paths, the deuterated sulfide

$(C_6H_5CD_2)_2S$, was synthesized (9) and subjected to kinetic study in the sulfide-sulfinic acid reaction (9). The deuterated compound was found to react with p-toluene-sulfinic acid at only about one-fifth the rate observed for benzyl sulfide. A kinetic isotope effect of this size requires that the carbon-deuterium bond be broken in the rate-determining step.



This occurs in equation 7b but not in equation 7a. It is therefore evident that equation 7b is the rate-determining step of the sulfide-sulfinic acid reaction. It has also been shown (9) that the ion formed in this reaction ($\text{RCH} = \overset{\oplus}{\text{S}}\text{CH}_2\text{R}$) undergoes almost instantaneous hydrolysis to the aldehyde and mercaptan as shown in equation 8, with the mercaptan then reacting almost as rapidly with some of the sulfinic acid remaining.



This last result makes it important to learn what sorts of products are formed when mercaptans react with

sulfinic acids. Obviously, this knowledge is essential for a complete understanding of the sulfide-sulfinic acid reaction. Despite the ease with which these substances react with each other under the proper conditions, there is practically nothing in the literature pertaining to this reaction, and the reaction has apparently never been studied under the conditions employed for the sulfide-sulfinic acid reaction. Therefore, the reaction of p-toluenesulfinic acid with some representative mercaptans has been investigated in acetic acid, and the results form one part of this thesis.

Also for more complete understanding of the sulfide-sulfinic acid reaction it was of interest to determine whether a secondary alkyl sulfide would undergo the same general type of reaction shown by the primary alkyl sulfide. Therefore product studies of the reactions of p-toluenesulfinic acid with isopropyl and 2-octyl sulfides were conducted. These form the second part of the thesis.

RESULTS

Reaction of Mercaptans with p-Toluenesulfinic Acid

In order that the results be as applicable to the sulfide-sulfinic acid reaction as possible, all the reactions were carried out in acetic acid-0.56 M water containing 0.6 M sulfuric acid. Except for isopropyl mercaptan, where its lower boiling point required a ten degrees lower reaction temperature, the reactions were run at 70°. Three different mercaptans, n-butyl, isopropyl and benzyl, were studied.

For a reaction run a quantity of sulfinic acid was dissolved in the acetic acid mixture, and the mercaptan, dissolved in a small amount of acetic acid, was rapidly added. Three minutes following this addition the reaction was quenched by pouring the solution into a large volume of water. The water insoluble products were extracted with ether. These products were first separated into individual fractions by alumina chromatography; then these fractions were separated into pure compounds by either fractional recrystallation or distillation depending upon whether the fraction was liquid or solid. The most important tool used in the final identification of the

products of the reaction was nuclear magnetic resonance.

p-Toluenesulfinic Acid-Butyl Mercaptan

Butyl mercaptan (90.0 mmoles) was reacted with p-toluenesulfinic acid (30.3 mmoles) under the conditions described above. Of the 12.8 g. of reactants 11.1 g. were recovered as products, or a 87% recovery of material. The only products of the reaction were butyl disulfide and p-tolyl butyl disulfide, in approximately equal molar quantities. After a series of purification steps 23.0 mmoles of butyl disulfide and 20.1 mmoles of p-tolyl butyl disulfide were obtained. The identity of the unsymmetrical disulfide was established by elemental analysis, molecular weight determination, and nuclear magnetic resonance spectroscopy.

p-Toluenesulfinic Acid-Isopropyl Mercaptan

Isopropyl mercaptan (91.0 mmoles) was reacted with p-toluenesulfinic acid (30.1 mmoles) under the same conditions as the above reaction. Of the 11.5 g. of reactants 9.5 g. were recovered as products, or an 84% recovery of material. The only products of the reaction were isopropyl disulfide and p-tolyl isopropyl disulfide, in approximately

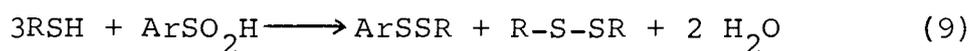
equal molar quantities. After a series of purification steps 21.4 mmoles of isopropyl disulfide and 20.7 mmoles of p-tolyl isopropyl disulfide were obtained. The structure of the unsymmetrical disulfide was established by the same techniques mentioned earlier for butyl p-tolyl disulfide.

p-Toluenesulfinic Acid-Benzyl Mercaptan

Benzyl mercaptan (20.4 mmoles) was reacted with p-toluenesulfinic acid (6.8 mmoles) under the conditions of the above two reactions. Of the 3.59 g. of reactants 2.43 g. were recovered as products. The only products of the reaction were benzyl disulfide and p-tolyl benzyl disulfide. From the crude product mixture a quantity of each of these two compounds large enough for identification was purified. But due to the similar nature of benzyl disulfide and p-tolyl benzyl disulfide quantitative separation of these two compounds was found inconvenient. The structure of the unsymmetrical disulfide was established by the same techniques mentioned earlier for butyl p-tolyl disulfide.

In all three cases the reactions were very rapid, with the reaction products always being the symmetrical

disulfide derived from the mercaptan and the unsymmetrical p-tolyl alkyl disulfide. When the Mercaptan was used in a 3:1 mole ratio to the sulfinic acid the molar amounts of the two disulfides produced were essentially the same. This suggests that under these reaction conditions the stoichiometry of the reaction is as follows:



The Reaction of Secondary Alkyl Sulfides with p-Toluenesulfinic Acid

The reaction of the secondary alkyl sulfides with p-toluenesulfinic acid was studied with two different sulfides, isopropyl sulfide and 2-octyl sulfide. The reactions were carried out at 70° in the same acetic acid-water-sulfuric acid solvent used for the mercaptan-sulfinic acid reaction studies. Preliminary kinetic studies of the behavior of the two alkyl sulfides by Mrs. E. Morkved showed that, under the conditions chosen for the reaction, 2.5 hours were required for the reaction to go to completion. The exact method of product work-up and identification varied slightly in the two cases. The details of both may be found in the Experimental section.

p-Toluenesulfinic Acid-Isopropyl Sulfide

p-Toluenesulfinic acid, 0.1 M (9.8 mmoles), was reacted with an excess of isopropyl sulfide (0.2 M). Originally it had been hoped to trap any volatile ketones which might be produced during the course of this reaction, in this case acetone. In order to do this the reaction mixture was swept with a stream of nitrogen. The nitrogen and any exhaust gases, which would include acetone, were then passed through a trap containing methanol cooled in dry ice. Following the reaction, treatment of the contents of the cold trap with 2,4-dinitrophenylhydrazine would provide the ketone derivative for both identification and an approximate yield. It was because of these reasons that the recovery of only 26 mg. of acetone 2,4-dinitrophenylhydrazone (0.11 mmoles) was very disappointing. However, upon testing the reaction system by dissolving 1.9 mmoles of acetone in the acetic acid-water-sulfuric acid mixture and sweeping with nitrogen under the same conditions as that of the reaction only 15.4 mg. of the acetone derivative was recovered. This represents only a 3.3% recovery of the acetone originally present in the reaction mixture.

Following the reaction of p-toluenesulfinic acid with

isopropyl sulfide the reaction mixture was poured into a quantity of distilled water. The water insoluble products were extracted from the aqueous solution with ether. The products were then separated and purified by alumina chromatograph. Besides the 26 mg. of acetone, 2,4-dinitrophenylhydrazone recovered from the cold trap, the reaction mixture yielded 4.1 mmoles of p-tolyl p-toluenethiolsulfonate and a quantity of unreacted sulfide. No other products were found, but it is possible that there may have been some disulfide recovered along with the sulfide. One can conclude from the recovery of some acetone 2,4-dinitrophenylhydrazone that acetone is definitely formed in the isopropyl sulfide-sulfinic acid reaction, but it is difficult to say how much.

p-Toluenesulfinic Acid-2-Octyl Sulfide

Because of the problems of determining the ketone yield in the isopropyl sulfide reaction, it was desired to examine a case where a more quantitative estimation of the ketone would be possible. 2-Octyl mercaptan was synthesized from 2-octanol. 2-Octyl sulfide was then synthesized by refluxing in methanol equimolar quantities of 2-octyl bromide with 2-octyl mercaptan in the presence of an excess

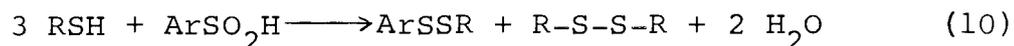
of potassium hydroxide. The sulfide was separated and purified by a series of distillations, and its purity and identity checked by elemental analysis.

p-Toluenesulfinic acid, 0.06 M (6.0 mmoles), was reacted with an excess of 2-octyl sulfide, 0.12 M (0.12 mmoles). Following the reaction, the reaction mixture was poured into a quantity of distilled water and the water insoluble products were extracted from the aqueous solution with ether. The ether was then removed and the separation of the reaction products was accomplished by alumina chromatography. p-Tolyl p-toluenethiolsulfonate (2.4 mmoles), and a crude fraction (0.28 g.) of 2-octanone were recovered as products along with a quantity of unreacted sulfide. These were the only products found, but it may be possible that some disulfides were recovered along with the sulfide. The 2-octanone was treated with 2,4-dinitrophenylhydrazine and the 2-octanone derivative recovered. Both the authenticity of the p-tolyl p-toluenethiolsulfonate and the 2-octanone 2,4-dinitrophenylhydrazone were proven by mixed melting point technique using known samples.

DISCUSSION

The Mercaptan-Sulfinic Acid Reaction

Isopropyl, butyl, and benzyl mercaptan were reacted with *p*-toluenesulfinic acid in acetic acid-0.56 M water-0.6 M sulfuric acid as the solvent. The details of the reaction conditions are given in the Experimental section. The reactions of the sulfinic acid with the mercaptans were all of the same general nature. All three of the mercaptans reacted rapidly with sulfinic acid to give equal molar quantities of two disulfides. The first of the disulfides was always the symmetrical disulfide derived from the mercaptan; the second disulfide was always the unsymmetrical *p*-tolyl alkyl disulfide. This suggests that under the reaction conditions used for this study the stoichiometry of the reaction is as follows:



The present reaction conditions involved rapid addition of three moles of the mercaptan to a solution of one mole of the sulfinic acid. These conditions are very different from those for any mercaptan-sulfinic acid reaction occurring during the course of the sulfide-sulfinic acid

reaction, because in the sulfinic acid-sulfide reaction the mercaptan is being formed slowly in the presence of an excess of sulfinic acid. In other work in this laboratory (9), Mrs. E. Morkved has tried to simulate the conditions for the latter process by adding dilute solutions of mercaptan relatively slowly to a solution containing an excess of the sulfinic acid. She found that by varying the speed and concentration at which the mercaptan was added it was possible to vary the stoichiometry of the sulfinic acid-mercaptan reaction. Slow addition of a dilute solution of the mercaptan gave a stoichiometry where 1.75 moles of sulfinic acid were consumed per mole of mercaptan. Rapid addition of twice as concentrated a solution led to consumption of only 0.80 moles of sulfinic acid per mole of mercaptan. It would appear that with the proper concentration and rate of addition of mercaptan the stoichiometry can be varied all the way from 3:1 to 1:3, as far as the sulfinic acid to mercaptan ratio is concerned. In order to bring the reaction ratio of mercaptan to sulfinic acid to less than 3:1, the mercaptan must be added to the solution in dilute quantities at a slow rate. In other words the concentration of unreacted mercaptan present in the reaction solution must never become really appreciable as

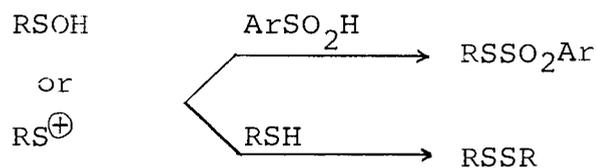
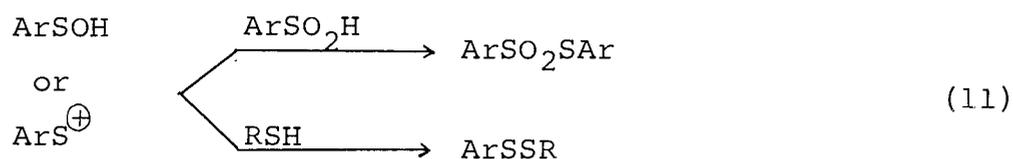
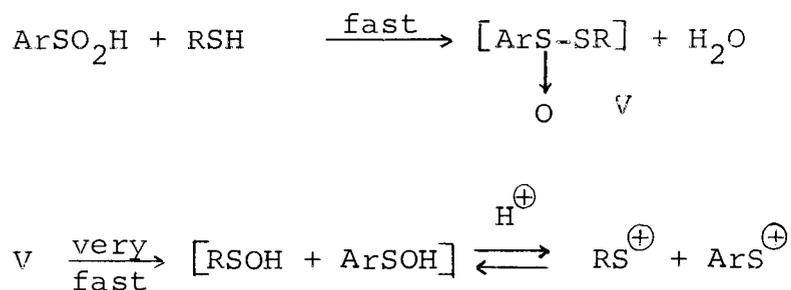
compared to the unreacted sulfinic acid present, if a 3:1 ratio of mercaptan to sulfinic acid is to be avoided. Morkved and Kice (9) also found that when the stoichiometry varied from the 3:1 molar ratio of mercaptan to sulfinic acid the products of the reaction were no longer completely disulfides but now consisted of a mixture of the two disulfides and the two thiolsulfonates, p-tolyl p-toluenethiolsulfonate and the appropriate alkyl p-toluenethiolsulfonate. For example, for a reaction of butyl mercaptan with p-toluenesulfinic acid, in which 1.72 moles of the sulfinic acid reacted per mole of mercaptan added, the products, in units of mole fraction of total products, were as follows: butyl disulfide 0.07; butyl p-tolyl disulfide 0.15; butyl p-toluenethiolsulfonate 0.42; p-tolyl p-toluenethiolsulfonate 0.36.

The literature reports that C. S. Marvel (11) reacted dodecanesulfinic acid (20 mmoles) with dodecyl mercaptan (20 mmoles). The solvent for the reaction was refluxing ether containing a trace of hydrochloric acid. The stoichiometry indicates the reaction of one mole of mercaptan with more than one mole of sulfinic acid. This is quite different from the 3:1 ratio of mercaptan to sulfinic acid reported in the thesis. Although Morkved and

Kice (9) did find comparable stoichiometry under some condition in their studies, there never was any mercaptan recovered unreacted. The main differences between Marvel's work and the studies in this laboratory are the much lower reaction temperature, and the much less acidic medium used for the reaction.

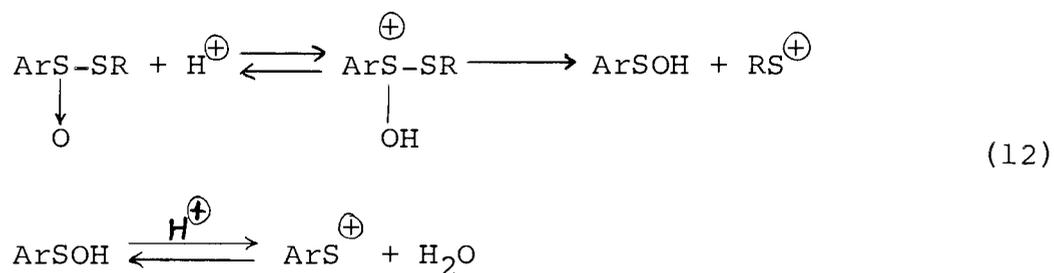
Mokved and Kice's findings (9) require a mechanism in which mercaptan reacts with sulfinic acid to form intermediates which are capable of reaction with either another mole of mercaptan or another mole of sulfinic acid. Capture of the intermediates by mercaptan results in the formation of disulfides; capture of sulfinic acid leads to thiolsulfonates. At equal concentrations of mercaptan and sulfinic acid capture by the mercaptan strongly predominates. Only when the concentration of mercaptan is much lower than that of the sulfinic acid can the sulfinic acid compete effectively. A possible scheme compatible with these findings would be one in which initial reaction of sulfinic acid with mercaptan leads, by one or more steps, to the sulfenic acids ArSOH and RSOH , or alternatively to the corresponding sulfenium ions ArS^{\oplus} and RS^{\oplus} . These sulfenic acids or ions then react even more rapidly with either mercaptan, giving disulfides, or sulfinic acid,

giving thiolsulfonates. This is shown below.



To accommodate Morkved and Kice's results (9) the first intermediate shown, the thiolsulfinate, must break down as fast as it is formed, and the sulfenic acids or sulfenium ions must react faster with the mercaptan than does sulfinic acid. If this were not true, all of the mercaptan would react with the sulfinic acid to form the first intermediate, and this would then subsequently decompose to products. This would not allow for the variation in products and stoichiometry with variation in mercaptan concentration that is found.

The difference Marvel noted in the stoichiometry might be caused by the thiolsulfinate not decomposing in ether at lower temperatures in the same manner as it does under the reaction conditions of this study. It is not inconceivable that rapid decomposition of the thiolsulfinate occurs in the very acidic acetic acid-sulfuric acid solution by an acid-catalyzed mechanism such as:



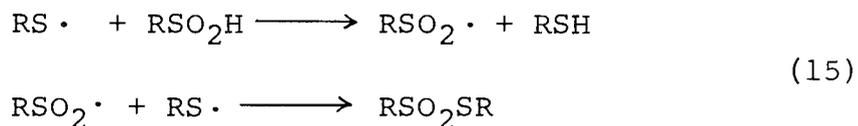
Vinkler and Klivenyi (14) have reported that decomposition of thiolsulfinate can be catalyzed by acids. But when a much more weakly acidic medium is used, as was the case in Marvel's study, the thiolsulfinate may decompose by a radical type mechanism.



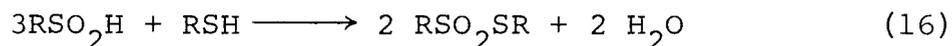
There is evidence from the work of Topping and Kharasch (12) on sulfinyl nitrates that sulfinyl radicals ($\text{RSO}\cdot$) when formed tend to react as follows:



Reaction of the $\text{RS} \cdot$ radicals with the sulfinic acid could occur in the manner shown below



The overall stoichiometry would then be as follows:

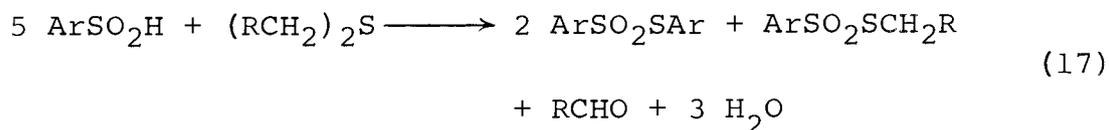


This stoichiometry is in agreement with the findings of Marvel.

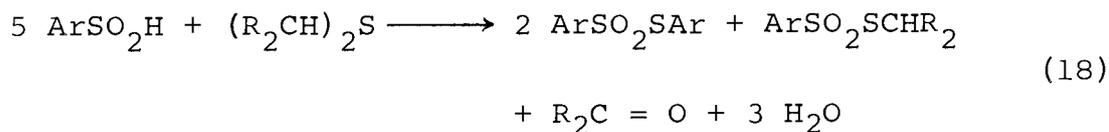
In any event it appears that the course and nature of the sulfinic acid-mercaptan reaction is dependent on solvent, acidity, and temperature. It would be of interest to study the reaction further under varying conditions. One interesting experiment would be to run the reaction at a much lower temperature in an attempt to isolate the first intermediate.

The Secondary Alkyl Sulfide-Sulfinic Acid Reaction

The study of Kice and Bowers and subsequent work by Mrs. E. Morkved have fairly well established that the normal stoichiometry of the primary alkyl sulfide-p-toluene-sulfinic acid reaction is as follows:



By analogy one might therefore expect the reaction of secondary alkyl sulfides with the same sulfinic acid to proceed in the same fashion.



In fact the isolated yields of p-tolyl p-toluenethiolsulfonate are in the right range for such a scheme; for the 2-octyl reaction 6.0 mmoles of sulfinic acid gave 2.4 mmoles of p-tolyl p-toluenethiolsulfonate, while in the isopropyl case 9.8 mmoles of sulfinic acid gave 4.1 mmoles of the same thiolsulfonate. However, so far no sec-alkyl p-toluenethiolsulfonate ($\text{ArSO}_2\text{SCHR}_2$) has been isolated. This, as shown by equation 18, should be one of the principal products of the sec-alkyl sulfide-sulfinic acid reaction. Several possible reasons may be suggested for the failure to isolate the sec-alkyl p-toluenethiolsulfonate.

First, since previous work has shown that lesser amounts of alkyl thiolsulfonates can sometimes be easily overlooked in the presence of larger amounts of p-tolyl p-toluenethiolsulfonate, it is possible that the

unsymmetrical thiolsulfonate went undetected in the isolation and identification of the thiolsulfonate fraction. This happened in the original work on the butyl sulfide-p-toluenesulfinic acid reaction. The only sure way to eliminate this possibility, since the infrared spectra are often not very informative in these systems, is by nuclear magnetic resonance examination of the thiolsulfonate fraction. This unfortunately was not done.

Second, although some thiolsulfonates can be chromatographed on alumina with no difficulty, others have been found to decompose on such treatment. It is quite possible this could happen with these sec-alkyl esters although it doesn't occur with the primary alkyl compounds. This possibility can be checked independently in future work.

Third, both butyl and benzyl p-toluenethiolsulfonate were stable to the strongly acidic medium of the reaction, but it is possible that the sec-alkyl p-toluenesulfonates will not be. This also can be checked by further independent experiments.

Unfortunately, no quantitative determination of the amount of ketone formed was conducted for either of the sec-alkyl sulfide studied. The crude yield of 2-octanone

from the sec-octyl sulfide reaction seems too large for the stoichiometry of equation 18. However, past experience shows that such yields are unreliable and that the only safe measurement of yield is to convert the ketone to the corresponding 2,4-dinitrophenylhydrazone and weigh the amount of solid derivative produced.

Any final decision as to whether there is a difference in stoichiometry between the primary alkyl sulfide and the secondary sulfide reactions must await more experimental evidence. Many of the above points must be checked. So far about all one can say with certainty is that the secondary alkyl sulfides react fairly readily with p-toluenesulfinic acid and that analogous to the primary alkyl sulfide-sulfinic reaction two of the major products are p-tolyl p-toluenethiolsulfonate and the ketone derived from oxidation of the secondary alkyl group of the sulfide.

EXPERIMENTAL

Materials

A solution of one percent water in acetic acid was prepared as follows. Glacial acetic acid was distilled from an excess of acetic anhydride. The content of the

acetic anhydride present in the acetic acid after distillation was determined by the procedure of Kilpi (10). An amount of water sufficient to remove the acetic anhydride and to bring the concentration of water present in the solution to one percent was then added quantitatively.

A 5 M solution of sulfuric acid in acetic acid-1% water was prepared from a portion of the above acetic acid and 100% sulfuric acid. Reagent grade sulfuric acid of approximately 95% was brought to 100% by the addition of 20% fuming sulfuric acid. The percent of sulfuric acid was determined by specific gravity.

Sodium p-toluenesulfinate was prepared by the procedure found in Organic Synthesis, Collected Volume I (2). The sodium p-toluenesulfinate was recrystallized from water twice and stored in this form. The p-toluenesulfinic acid was prepared from the salt by the procedure of Kice and Bowers (7).

Isopropyl sulfide, isopropyl mercaptan, and n-butyl mercaptan were obtained from Wateree Chemical Company, Inc. Benzyl mercaptan was obtained from Eastman Organic Chemicals. All were distilled before use.

2-Octyl sulfide was prepared as follows. 2-Octyl mercaptan was prepared from the 2-octyl alcohol by the

procedure of Frank (1). This mercaptan was dissolved in three times its volume of methanol under a nitrogen atmosphere, and an equimolar quantity of potassium hydroxide dissolved in methanol was added. An equimolar quantity of sec-octyl bromide was then added dropwise with stirring. The reaction mixture was allowed to reflux for 10 hours. The sulfide was separated and purified by a series of distillations, b.p. 109° (3 mm).

Anal. Calculated for $C_{16}H_{34}S$: C, 74.45%; H, 13.22%.

Found: C, 74.42%; H, 13.22%.

Product Study of the Sulfinic Acid-Mercaptan Reaction

General Procedure

The general procedure was as follows. A three-neck round-bottom flask was fitted with a condenser, dropping funnel, and a gas capillary by which nitrogen could be bubbled through the reaction mixture. The condenser was connected by tubing to a mineral oil trap which prevented back diffusion of air into the system.

An 0.6 M solution of sulfuric acid in acetic acid-1% water was prepared from the two starting acetic acid solutions. From five to ten mmoles of p-toluenesulfinic acid was dissolved in 100 ml. of this solution. The air

was then removed from the solution in the reaction vessel by the slow bubbling of purified nitrogen through the solution. The reaction vessel was then placed in a mineral oil bath at 70° , and was allowed to warm seven minutes. At this time 3.0 mmoles of mercaptan per mmole of p-toluenesulfinic acid was rapidly added with vigorous stirring. For the addition, the mercaptan was dissolved in an equal volume of acetic acid-1% water. Three minutes after the addition of the mercaptan, the reaction solution was poured into one liter of distilled water. This solution was extracted with three 200-250 ml. portions of ether, and the ether solution was then washed with several portions of sodium carbonate; it was then washed with distilled water, and dried over anhydrous magnesium sulfate. Most of the ether was removed under reduced pressure at room temperature. The residue was taken up in a small amount of hexane and placed on a column of 75 grams of acid-washed alumina. The column was eluted with the following solvents: 400 ml. hexane; hexane-benzene, 100 ml. 10:1; 100 ml. 1:1, 100 ml. 1:10; 100 ml. benzene; 1:1, benzene-ether, 100 ml. ether, 100 ml. Fractions of 50 ml. volume were collected and evaporated almost to dryness on a steam bath. The residues were then taken up with

ether and placed under vacuum to remove the last of the solvent.

n-Butyl Mercaptan-p-Toluenesulfinic Acid

From the reaction of butyl mercaptan (8.12 g.) with p-toluenesulfinic acid (4.74 g.), 11.1 g. of product was obtained in the residues of the hexane fractions of the chromatography. The product appeared to be a mixture, and by micro-distillation two major fractions could be separated. Fraction I (4.1 g.) had a boiling point of 53-55° (0.6 mm.), the same as n-butyl disulfide. Its index of refraction was 1.4903, as compared to 1.4900 for a known sample of n-butyl disulfide. Fraction II (3.9 g.) had a boiling point of 102-104° (0.6 mm.), and an index of refraction of 1.5657. The rest of the 11.1 grams of material was divided among forerun, cuts between fractions, and residues.

For the purposes of identification, p-tolyl disulfide was prepared as follows. p-Tolyl mercaptan was prepared by the reduction of p-toluenesulfonyl chloride with zinc dust and sulfuric acid by the procedure found in Organic Synthesis, Volume I (3). The mercaptan was then oxidized to the disulfide using a methanol solution of iodine. The

disulfide was purified by a series of recrystallizations from methanol, and dried under vacuum. The melting point, 48° , agreed with the literature (4).

Nuclear magnetic resonance spectra were obtained of n-butyl disulfide, p-tolyl disulfide, and Fraction II. Each of the peaks in the spectrum of Fraction II was similar to one of the peaks in the spectra of either n-butyl disulfide or p-tolyl disulfide, but each peak's area was only one-half that for the same peak in the symmetrical disulfides. Integration of the spectrum of Fraction II indicated four aromatic hydrogens, two hydrogens attached to the carbon next to the sulfide linkage, three hydrogens in the methyl of a tolyl group, and seven remaining hydrogens in an n-butyl group. The spectrum of Fraction II is one that might be expected from p-tolyl n-butyl disulfide. Fraction II was subjected to analysis and molecular weight determination.

Anal. Calculated for $C_{11}H_{16}S_2$: C, 62.30% H, 7.59%.

Mol. Wt. 212, Found: C, 62.20%; H, 7.72% Mol. Wt.

(osmometric in $CHCl_3$) 210.

Isopropyl Mercaptan-p-Toluenesulfinic Acid

Because the boiling point of isopropyl mercaptan is 68° (5), the reaction was carried out at 60° instead of the usual 70° . From the reaction of isopropyl mercaptan (6.8 g.) with p-toluenesulfinic acid (4.7 g.), 9.5 g. of product were obtained in the residues of the hexane fractions of the chromatography. By micro-distillation two major fractions could be separated. Fraction I (3.5 g.) had a boiling point of 23° (0.6 mm.), the same as a sample of isopropyl disulfide which was prepared by the oxidation of isopropyl mercaptan with a methanol solution of iodine. The index of refraction of Fraction I was 1.4894 as compared to 1.4890 for the known sample of isopropyl disulfide. Fraction II (4.1 g.) had a boiling point of $93-94^{\circ}$ (0.1 mm.) and an index of refraction of 1.5738. The rest of the 9.5 grams of product was divided among forerun, cuts between fractions, and residue.

Nuclear magnetic resonance spectra were obtained of isopropyl disulfide and of Fraction II. Each of the peaks in the spectrum of Fraction II was similar to one of the peaks in the spectra of either isopropyl disulfide or p-tolyl disulfide, but each peak's area was only

one-half that for the same peak in the symmetrical disulfides. Integration of the spectrum of Fraction II indicated four aromatic hydrogens, one hydrogen attached to a carbon next to the sulfide linkage, three hydrogens in the methyl of a tolyl group, and six hydrogens in the methyl carbons of an isopropyl group. The spectrum of Fraction II is one that might be expected from p-tolyl n-butyl disulfide. Fraction II was subjected to analysis and molecular weight determination.

Anal. Calculated for $C_{10}H_{14}S_2$: C, 60.50%; H, 7.12%.

Mol. Wt. 198. Found: C, 60.60%; H, 7.12%, Mol. Wt.

(osmometric in $CHCl_3$) 195.

Benzyl Mercaptan-p-Toluenesulfinic Acid

Benzyl mercaptan was the first to be used in this series. From the first reaction of benzyl mercaptan (2.33 g.) with p-toluenesulfinic acid (1.39 g.), 2.76 g. of product was obtained in the residues of the hexane fractions of chromatography. From the second reaction of benzyl mercaptan (2.53 g.) with p-toluenesulfinic acid (1.06 g.), 2.43 g. of material were recovered from the hexane fraction residues. The residues appeared to be a mixture of two products, and by fractional recrystallation

two compounds were separated. Fraction I had a melting point of 73° , which is the same as benzyl disulfide (4). A mixed melting point with a known sample of benzyl disulfide showed no depression. Fraction II had a melting point of $34-35^{\circ}$.

Nuclear magnetic resonance spectra were obtained of benzyl disulfide, and Fraction II. Each of the peaks in the spectrum of Fraction II was similar to one of the peaks in the spectra of either benzyl disulfide or *p*-tolyl disulfide, but each peak's area was only one-half that for the same peak in the symmetrical disulfides. There was shift of 0.32τ units in the peak due to the hydrogens attached to the carbon next to the sulfur linkage.

Integration of the spectrum of Fraction II indicated nine aromatic hydrogens, two hydrogens on the methylene carbon of a benzyl group, and three hydrogens attached to the methyl carbon of a *p*-tolyl group. The spectrum of Fraction II is one that might be expected from *p*-tolyl benzyl disulfide. Fraction II was subjected to analysis and molecular weight determination.

Anal. Calculated for $C_{14}H_{14}S_2$: C, 68.24%; H, 5.72%.

Mol. Wt. 246. Found: C, 68.68%; H, 5.77%. Mol.Wt.

(osmometric in $CHCl_3$) 248.

Product Study of the Sulfinic Acid-Secondary Alkyl Sulfide
Reaction General Procedure

A reaction vessel as described by Kice and Bowers (6) was used. Between the condenser and oil trap was placed a cold trap. This contained methanol and was cooled in dry ice. The exhaust gases from the reactions were passed through the methanol. Five to ten millimoles of p-toluenesulfinic acid and approximately twice that number of millimoles of the alkyl sulfide were dissolved in 100 ml. acetic acid-1% water containing 0.6 M sulfuric acid. The solution was placed into the reaction vessel, and the air was removed from the vessel by the slow bubbling of purified nitrogen through the solution. The reaction vessel was placed in a constant temperature bath at 70° for 2.5 hours. The reaction solution was then worked up in the same manner as described earlier for the reaction solution from the sulfinic acid-mercaptan reaction. The methanol from the cold trap was treated with 2,4-dinitrophenylhydrazine for the detection of volatile ketones

Isopropyl Sulfide-p-Toluenesulfinic Acid

From a reaction employing 1.51 grams of p-toluenesulfinic acid and 2.5 grams of isopropyl sulfide, the benzene fraction from the chromatography gave 1.03 grams of p-tolyl p-toluenethiolsulfonate, m.p. 76°. This melting point agrees with the literature (4). Treatment of the methanol solution in the cold trap with 2,4-dinitrophenylhydrazine in the usual manner gave 26 mg. of acetone 2,4-dinitrophenylhydrazone, m.p. 126°. A test, in which a known amount of acetone was dissolved in the acetic acid-water-sulfuric acid solution used and was then subjected to the reaction conditions, showed that only 3.3% of the acetone present was carried into the trap and precipitated as the 2,4-dinitrophenylhydrazone. Both the authenticity of the p-tolyl p-toluenethiolsulfonate and the acetone 2,4-dinitrophenylhydrazone were proven by the mixed melting point technique using known samples.

2-Octyl Sulfide-p-Toluenesulfinic Acid

The reaction of 2.68 grams of 2-octyl sulfide and 0.96 grams of p-toluenesulfinic acid gave the following products from the chromatography: From the hexane

fractions, 1.54 g. of unreacted 2-octyl sulfide; from the hexane-benzene fraction, 0.28 g. of crude 2-octanone; and from the benzene fraction 0.68 g. of p-tolyl p-toluenethiolsulfonate. There was also a total of 0.31 g. of yellow oil as a residue in the last fraction (ether through methanol).

The 2-octanone was treated with 2,4-dinitrophenylhydrazine in the usual manner, giving a derivative, m.p. 59°. The identity of the derivative was confirmed by a mixed melting point with an authentic sample of 2-octanone 2,4-dinitrophenylhydrazone.

SUMMARY

1. Alkyl mercaptans react very rapidly with p-toluenesulfinic acid, when the mercaptan is added rapidly in high concentrations to a solution of sulfinic acid dissolved in an acetic acid-0.56 M water-0.6 M sulfuric acid solvent at 70°. The mercaptan will consume one mmole of sulfinic acid for every three mmole of mercaptan added; the reaction products are two disulfides, the first being the symmetrical disulfide derived from the mercaptan, the second being the unsymmetrical alkyl p-tolyl disulfide.

2. Secondary alkyl sulfides react with p-toluene-sulfinic acid at 70° in an acetic acid-0.56 M water-0.6 M sulfuric acid solvent. The products of the reaction so far identified are p-tolyl p-toluenethiolsulfonate and the ketone derived from oxidation of the secondary alkyl group of the sulfide.

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