

AN ABSTRACT OF THE THESIS OF

NORMAN EDWARD PAWLOWSKI for the DOCTOR OF PHILOSOPHY
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TITLE THE MECHANISMS OF THE SCISSION OF SOME SULFUR -
SULFUR BONDS

I. THE THERMAL DECOMPOSITION OF SULFINYL SULFONES

II. THE THERMAL DECOMPOSITION OF THIOLSULFONATES

III. THE ACID HYDROLYSIS OF BUNTE SALTS

Abstract approved _____ Signature redacted for privacy.
(Major professor)

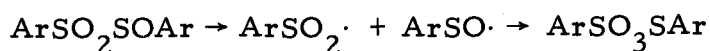
I. THE THERMAL DECOMPOSITION OF SULFINYL SULFONES

The mechanism of the thermal decomposition aromatic sulfinyl sulfones and the mechanism of their reaction with aromatic sulfinic acids has been determined.

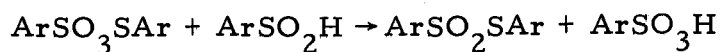
The rate of decomposition of p-toluenesulfinyl p-tolyl sulfone, II, is unaffected by the presence of added sulfinic acid. Reaction with sulfinic acid occurs by the rate-determining unimolecular decomposition of II into intermediates which then react with any sulfinic acid present to form thiolsulfonate and sulfonic acid. In the absence

of added sulfinic acid the intermediates from the decomposition of II undergo further reaction to form disulfide, thiolsulfonate and sulfonic acid.

The rate of decomposition of aromatic sulfinyl sulfones is little affected by either the solvent or the nature of the aryl group. Trapping of $\text{ArSO}_2\cdot$ radicals by added olefin and experiments with galvinoxyl, a stable free radical used for detecting and counting free radicals, shows that the decomposition involves the homolytic scission of the sulfur-sulfur bond into $\text{ArSO}_2\cdot$ and $\text{ArSO}\cdot$ radicals. The trapping of a ArS^+ ion by added olefin is evidence that even in the presence of a radical trap some of the $\text{ArSO}_2\cdot$ and $\text{ArSO}\cdot$ radicals undergo cage recombination to form a sulfenyl sulfonate. The sulfenyl

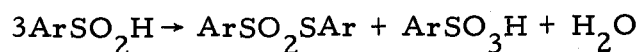


sulfonate reacts with any sulfinic acid present,

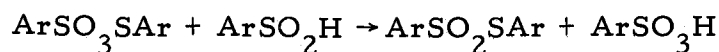
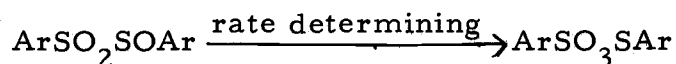
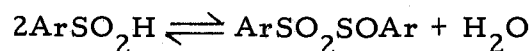


or in the absence of sulfinic acid it undergoes further decomposition to form disulfide, thiolsulfonate and sulfonic acid.

Sulfinyl sulfones have been postulated to be the key intermediate in the disproportionation of aromatic sulfinic acids (12, 42).



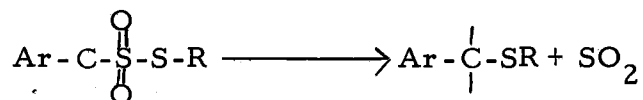
The mechanism proposed by Kice and co-workers (42, 45) is confirmed by the present work.



The homolytic scission of the sulfur-sulfur bond in sulfinyl sulfones is much more facile than the same process in disulfide, thiolsulfinates, thiolsulfonates or α -disulfones.

II. THE THERMAL DECOMPOSITION OF THIOLSULFONATES

The thermal decomposition of aralkanethiolsulfonates



has been investigated.

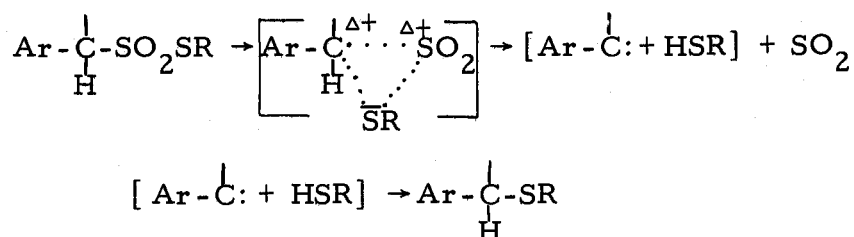
Experiments with the stable free radical galvinoxyl indicate that free radicals are not involved in the decomposition to any significant extent.

Partial decomposition of mixtures optically active phenyl α -toluenethiolsulfonate- α -d, XXV- α -d, and non-deuterated XXV followed by recovery of the undecomposed thiolsulfonate and measurement of its optical activity shows that the decomposition does not exhibit a

kinetic isotope effect.

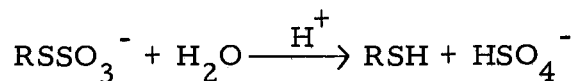
Other investigators have found that the transition state of the decomposition of thioisulfonates possesses partial negative charge on the sulfide sulfur, partial positive charge on the aralkane group (44, 46, 47), and that the decomposition of optically active XXV-a - d occurs with a high degree of racemization (32).

In light of the above results the following is suggested as a possible mechanism:



III. THE ACID HYDROLYSIS OF BUNTE SALTS

The acid hydrolysis of Bunte salts, S-alkyl thiosulfates, has been investigated.



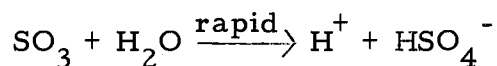
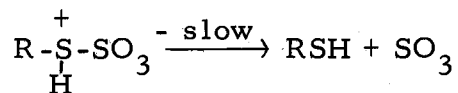
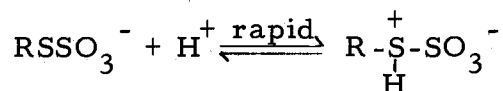
Kinetic studies of the hydrolysis of sodium S-benzyl thiosulfate, XXX, were carried out in mixtures of 40, 60 and 80 percent dioxane-water. The rate of hydrolysis was found to increase markedly as the percent dioxane increased although the enthalpy of activation changed very little. The increased rate is thus due to the entropy of activation becoming more positive as the dielectric constant of

the medium is decreased.

The rate of hydrolysis of sodium S-ethyl thiosulfate was measured in 1.00 N DCl-D₂O, and, under otherwise identical conditions, in 1.00 N HCl-H₂O. The hydrolysis rate was found to be 1.4 times faster in the deuterated solvent.

The rates of hydrolysis of several substituted S-aryl thiosulfates indicate that the ArS- group has a lower electron density on sulfur in the transition state of the rate determining step than it has in the reactants.

The possible mechanisms for the hydrolyses of the various known compounds of the type Y-SO₃⁻ are discussed and data on the hydrolysis of several of these is reviewed. The significance of the solvent isotope effect is also discussed. The following mechanism is proposed for the hydrolysis of Bunte salts:



THE MECHANISMS OF THE SCISSION OF SOME
SULFUR-SULFUR BONDS

- I. THE THERMAL DECOMPOSITION OF SULFINYL SULFONES
- II. THE THERMAL DECOMPOSITION OF THIOLSULFONATES
- III. THE ACID HYDROLYSIS OF BUNTE SALTS

by

NORMAN EDWARD PAWLOWSKI

A THESIS

submitted to

OREGON STATE UNIVERSITY

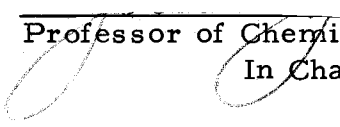
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degree of

DOCTOR OF PHILOSOPHY

June 1966


APPROVED:

Signature redacted for privacy.



Professor of Chemistry
In Charge of Major

Signature redacted for privacy.



Chairman of Department of Chemistry

Signature redacted for privacy.

Dean of Graduate School

Date thesis is presented

Sept. 30, 1965

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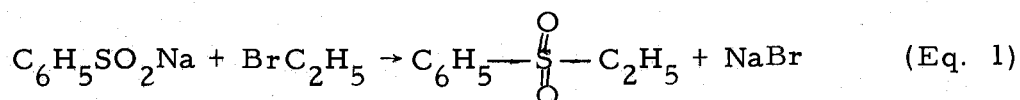
THE MECHANISMS OF THE SCISSION OF SOME SULFUR-SULFUR BONDS

I. THE THERMAL DECOMPOSITION OF SULFINYL SULFONES

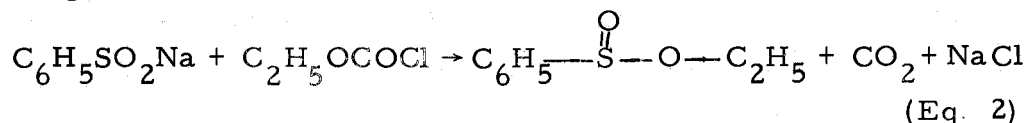
INTRODUCTION

Organic acids containing sulfur have long been known. In 1877 Pauly and Otto (66) suggested nomenclature for these, the compounds of the form ArSO_2H being named sulfinsäure or sulfinic acids.

In this early investigation of sulfinic acids, sodium benzene sulfinate was reported (58) to react with bromoethane (Eq. 1) to form the corresponding sulfone. Shortly thereafter sodium benzene sulfinate was reported to form a sulfinate ester when reacted with



a halide, ethyl chlorocarbonate (Eq. 2). Otto (63) correlated this conflicting data on the mode of reaction of sulfinates by suggesting



that sulfinates may behave as two "tautomers," $\text{Ar}\overset{\text{O}}{\underset{\text{O}}{\text{S}}}\text{Na}$ and $\text{Ar}\overset{\text{O}}{\text{S}}(\text{O})\text{Na}$, with either the sulfur or one of the oxygen atoms acting as a nucleophile.

This left open the question as to the position of the proton in sulfinic acids, whether it exists on the sulfur, $\text{Ar}\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{H}$, or on the

oxygen, $\text{Ar}\overset{\text{O}}{\underset{\text{O}}{\text{S}}}\text{OH}$, as in most acids. Guryanova and Syrkin (37) measured the dipole moments of several sulfinic acids in dioxane and benzene. Their values are in better agreement with the values calculated for the structure $\text{Ar}\overset{\text{O}}{\underset{\text{O}}{\text{S}}}\text{H}$ than for $\text{Ar}\overset{\text{O}}{\text{S}}-\text{OH}$. However, their calculated values were made from planar models, an erroneous approximation since both sulfonates (34) and sulfones (74) have been shown to be pyramidal.

Bredereck and co-workers (10) studied the ultraviolet spectra of sulfinic acids in polar and nonpolar solvents. By comparison of their spectra with those of sulfones and sulfonate esters they concluded that the structure for sulfinic acid is with the proton on the oxygen, $\text{Ar}\overset{\text{O}}{\text{S}}-\text{OH}$.

Detoni and Hadzi (31) made a thorough study of the infrared and Raman spectra in solid form and in solution of sulfonic acids, sulfonate esters, sulfoxides, sulfones and deuterated and non-deuterated sulfinic acids. Their results leave little doubt as to the correctness of the structure with the proton on the oxygen, $\text{Ar}\overset{\text{O}}{\text{S}}-\text{OH}$.

In 1866 Otto and Ostrop (61) reacted phosphorus pentachloride with benzenesulfinic acid to prepare benzenesulfinyl chloride. They isolated a side product of the formula $\text{C}_{12}\text{H}_{10}\text{S}_2\text{O}_3$ but failed to recognize it as the sulfinic anhydride. Forty-two years later Knoevenagel and Polack (52) identified it as the sulfinic anhydride and published both a procedure for its preparation and data on the

physical properties of several sulfinic acid anhydrides. Their preparation consisted of dehydrating the corresponding sulfinic acid in acetic acid with concentrated sulfuric acid and acetic anhydride. This method has the disadvantage of producing an impure product that turns brown upon standing and decomposes if recrystallization is attempted.

Bredereck and co-workers (7, p. 61; 11) developed a greatly improved procedure for the preparation of sulfinic acid anhydrides. They slowly mixed stoichiometric amounts of the anhydrous sodium sulfinate with the sulfinyl chloride in dry ether. Recrystallization of the product was avoided by triturating it with water and ether, filtering and drying in a vacuum desiccator. By this method the product is a white solid melting about ten degrees higher than that obtained by Knoevenogel and Polack's method. Infrared analysis proves that the products from both methods are identical.

By use of infrared spectroscopy Bredereck and co-workers (7, p. 29-31; 11) demonstrated that sulfinic acid anhydrides were actually sulfinyl sulfones, $\text{Ar}\overset{\text{O}}{\underset{\text{O}}{\parallel}}\text{S}-\overset{\text{O}}{\parallel}\text{S}-\text{Ar}$, and not true acid anhydrides as previously believed. The basis for this structural assignment is as follows: In the sulfur-oxygen region of the infrared spectrum there are no absorption bands other than those assigned to the sulfinyl and sulfone groups. Thus, p-toluenesulfinyl p-tolyl sulfone, II, has strong absorption at 1096 cm^{-1} and 1322 cm^{-1} which is assigned

to the sulfone group, $\begin{array}{c} \text{O} \\ \parallel \\ -\text{S}- \\ \parallel \\ \text{O} \end{array}$. If the compound had the normal anhydride structure no sulfone group would be present in the molecule. Comparison of the infrared spectra of thiolsulfinates, thiolsulfonates, α -disulfones, and disulfides with the spectrum of the corresponding sulfinyl sulfone shows the presence of both sulfinyl and sulfone bands. On the other hand, there is no similarity in the sulfur-oxygen region between sulfinyl sulfones and alkyl sulfinates or alkyl sulfonate esters. This lack of similarity rules out the structures $\text{Ar}\overset{\text{O}}{\parallel}\text{S}-\text{O}-$ and $\text{Ar}\overset{\text{O}}{\parallel}\text{S}-\text{O}$ as possible structural groups in sulfinic acid anhydrides.

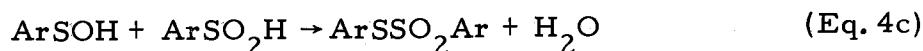
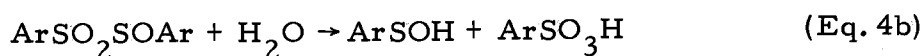
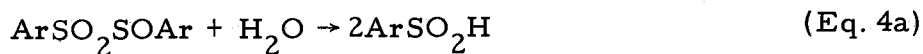
Early in the history of sulfinic acids they were reported (59, 60, 65, 66) to undergo an unusual disproportionation (Eq. 3) which was thought to be an equilibrium since it was suppressed by water. The reaction was quickly recognized (65) to be a useful method for



the preparation of aryl arenethiolsulfonates.

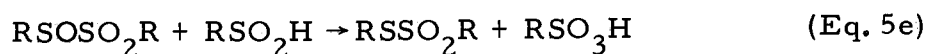
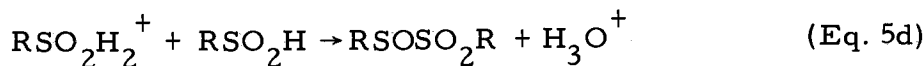
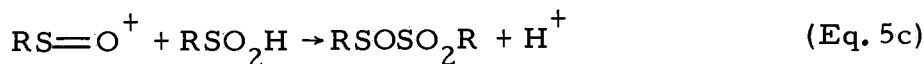
On the basis of the greater instabilities of sulfinyl sulfones than sulfinic acids and because these two compounds give similar decomposition products, Knoevenagel and Polack (52) suggested that sulfinic acids decompose via the sulfinyl sulfone. Upon hydrolyzing their sulfinyl sulfone with water, they obtained not only the sulfinic acid but also thiolsulfonate (no doubt from partial decomposition during the preparation). Therefore, they reasoned that there were

two reactions between water and sulfinyl sulfone, Eq. 4a and Eq. 4b. The sulfenic acid produced in Eq. 4b reacts with sulfinic acid present



to form the thiolsulfonate.

Bredereck and co-workers (7, 12, 13) studied the mechanism of the disproportionation in non-aqueous media. They found the reaction to be acid catalyzed; thus, the sulfonic acid formed in the products gives the disproportionation an autocatalytic nature. They failed to correlate its rate with acidity, nor did they ascertain its dependence upon water concentration. They noted that the rate decreases with increased solvent basicity and concluded that RSO_2H_2^+ was the reactive species. They postulated that the mechanism of the disproportionation involves the following reactions:



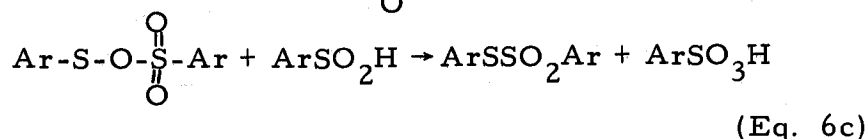
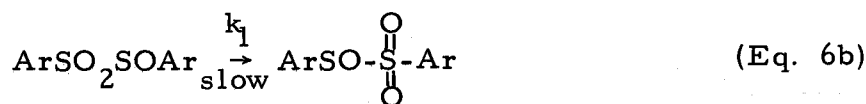
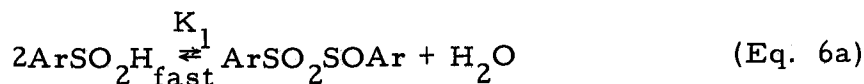
In this scheme sulfinyl sulfone is the key intermediate, and reacts

directly with sulfinic acid to form the products. They theorized that this product forming reaction (Eq. 5e) is at least 20 times faster than the disproportionation of the sulfinic acid. To support this theory, they mixed equal molar quantities of p-toluenesulfinyl p-tolyl sulfone and p-toluene-sulfinic acid and isolated the corresponding thiolsulfonate in 68 percent yield.

Allen and Reich (2) studied the disproportionation of p-toluenesulfinic acid in aqueous solution. Their data was collected using potassium iodide as a catalyst. It has since been shown that iodide reacts with thiolsulfonates (7, p. 62), one of the reaction products, to give disulfides which are now known to react with sulfinic acids (43). Therefore, no mechanistic conclusions can be drawn from their data.

Kice and co-workers (42, 45) investigated the mechanism of the disproportionation of sulfinic acids in acetic acid containing various amounts of water and sulfuric acid. They found the rate of disproportionation to be second order in sulfinic acid, strongly retarded by added water, slightly increased by added sulfuric acid, and to exhibit a small negative salt effect. With para-substituted benzenesulfinic acids the rate is accelerated by electron-donating substituents and retarded by electron-withdrawing ones. They showed that in these acetic acid-water-sulfuric acid mixtures the rate of hydrolysis of p-toluenesulfinyl p-tolyl sulfone is extremely

rapid. Also, they showed that any reaction between p-toluenesulfinic acid and p-toluenesulfinyl p-tolyl sulfone is not rapid enough to compete with this hydrolysis. Considering these results, the pronounced retardation by water, the rather small effect of added strong acid, the second-order kinetics in sulfinic acid, and the rapid hydrolysis of sulfinyl sulfone, Kice and co-workers felt that any direct reaction between sulfinic acid and sulfinyl sulfone, as proposed by Brederick and co-workers (12), cannot be significantly involved in the disproportionation of sulfinic acids. Instead, they favored a mechanism involving a highly unfavorable initial equilibrium between sulfinic acid and sulfinyl sulfone (Eq. 6a) followed by a rate-determining decomposition of sulfinyl sulfone (Eq. 6b). Such a decomposition of the sulfinyl sulfone is consistent with the observation (12, 42, 52) that it decomposes during all attempts at recrystallization, but no study of the nature of sulfinyl sulfone had been made. For the products of this decomposition Kice and co-workers suggested a rearrangement to a mixed sulfenic-sulfonic anhydride, Ar-S-O-S(=O)-Ar (Eq. 6b). This intermediate would then undergo further reaction



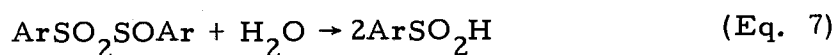
with sulfinic acid to form the products, sulfonic acid and thiosulfonate (Eq. 6c). They pointed out that there were other mechanistic schemes consistent with the kinetic data, but that this one seemed by far the most plausible.

Although there is disagreement on the details of the mechanism of the disproportionation of sulfinic acids, all of the workers have postulated sulfinyl sulfone as one of the key intermediates. Data regarding the behavior of sulfinyl sulfones is scant and incomplete. The intent of the first part of the present work was to obtain sufficient evidence as to the nature of sulfinyl sulfones and their reaction with sulfinic acids so to be able to distinguish between the mechanism suggested by Brederick and co-workers and that suggested by Kice and co-workers.

RESULTS

Kinetics of the Thermal Decomposition
of p-Toluenesulfinyl p-Tolyl Sulfone

Since aromatic sulfinyl sulfones are readily hydrolyzed to two molecules of the corresponding sulfinic acid (Eq. 7), their



thermal decomposition may be studied only in anhydrous media.

However, this ease of hydrolysis allows one to follow the kinetics of the decomposition of sulfinyl sulfones by withdrawing 5 ml. aliquots from the decomposition apparatus directly into an equal volume of cold 1.5 N sulfuric acid. The liberated sulfinic acid is diluted to 25 ml. with 1.5 N sulfuric acid and immediately titrated with 0.1 M sodium nitrite (42). The sodium nitrite is added using a 10 ml. microburet with its tip below the surface of the solution, which is stirred with a Teflon-covered magnetic stirring bar. After each addition of sodium nitrite solution a small drop is removed and touched to a strip of potassium iodide-starch test paper. The endpoint of the titration is reached when a drop produces a faint pink color on the potassium iodide-starch paper within five seconds. Following the disappearance of sulfinyl sulfone in this manner insures that the kinetics are a measure of the disappearance of sulfinyl sulfone by its thermal decomposition, since the loss of any sulfinyl

sulfone due to hydrolysis by any moisture in the reaction apparatus would not decrease the apparent sulfinyl sulfone titer.

Control experiments showed that the rate of disproportionation of any sulfinic acid in the reaction solution is quite slow compared to the decomposition rate of sulfinyl sulfone and during runs where there was a large concentration of added sulfinic acid corrections can be made for its loss due to the normal disproportionation.

In the present work the stability of p-toluenesulfinyl p-tolyl sulfone, II, was first carefully measured in anhydrous dioxane. It was found to undergo a rate-determining unimolecular decomposition with a half-life of about 25 minutes at 50° C. A plot of the logarithm of the concentration against time shows that the decomposition follows good first-order kinetics. These kinetics are strictly first-order throughout the entire course of the decomposition and the rate is unaffected by initial concentration. No variation from this was ever found while investigating the decomposition over a wide range of temperatures and in three widely differing solvents. A summary of these kinetics is shown in Tables I, II, and III.

Kinetics of the Thermal Decomposition of p-Toluenesulfinyl p-Tolyl Sulfone in the Presence of p-Toluenesulfinic Acid

As just mentioned, in anhydrous dioxane p-toluenesulfinyl p-tolyl sulfone in the absence of added sulfinic acid decomposes with

Table I. Kinetics of the Decomposition of p-Toluenesulfinyl p-Tolyl Sulfone in Dioxane.

Temp. °C	(II) M	(CH ₃ C ₆ H ₄ SO ₂ H) M	k ₁ × 10 ⁴ sec. ⁻¹
29.3	0.05	0.00	0.206
29.3	0.05	0.00	0.214
29.3	0.05	0.00	0.21
39.5	0.05	0.00	1.03
39.5	0.05	0.00	1.03
39.5	0.05	0.00	0.968
49.3	0.05	0.101	4.0
49.3	0.047	0.050	3.8
49.3	0.05	0.00	3.9
49.3	0.05	0.00	3.8
50.8	0.05	0.00	4.5
50.8	0.05	0.052	4.6
50.8	0.05	0.00	4.7
50.8	0.053	0.00	4.6
50.8	0.025	0.00	4.8
51.8	0.052	0.051	5.2
51.8	0.053	0.00	5.5
51.8	0.05	0.100	5.0
51.8	0.05	0.050	5.0
51.8	0.05	0.00	5.2
51.8	0.05	0.05	5.2

$$\Delta H^\ddagger = 27.8 \text{ Kcal. /mole}$$

$$\Delta S^\ddagger = +11.7 \text{ e.u.}$$

Table II. Kinetics of the Decomposition of p-Toluenesulfinyl
p-Tolyl Sulfone in Acetonitrile.

Temp. °C	(II) M	(CH ₃ C ₆ H ₄ SO ₂ H)	$k_1 \times 10^4$ sec. ⁻¹
24.3	0.052	0.00	0.402
24.3	0.051	0.00	0.402
39.5	0.053	0.00	1.43
39.5	0.056	0.00	1.47
39.5	0.05	0.050	1.22
39.5	0.05	0.00	1.27
39.5	0.05	0.00	1.5
49.3	0.051	0.05	4.6
49.3	0.05	0.00	5.6
49.3	0.053	0.00	5.3
49.3	0.05	0.05	3.5

$$\Delta H^\ddagger = 25.7 \text{ kcal. /mole}$$

$$\Delta S^\ddagger = +5.5 \text{ e. u.}$$

Table III. Kinetics of the Decomposition of p-Toluenesulfinyl
p-Tolyl Sulfone in Acetic Acid.

Temp. °C	(II) M	(CH ₃ C ₆ H ₄ SO ₂ H)	$k_1 \times 10^4$ sec. ⁻¹
29.3	0.05	0.00	0.268
29.3	0.05	0.00	0.258
49.3	0.025	0.00	4.5
49.3	0.05	0.00	4.5
49.3	0.05	0.00	8.0
49.3	0.009	0.00	6.0
49.3	0.05	0.00	6.6

$$\Delta H^\ddagger = 28.2 \text{ Kcal. /mole}$$

$$\Delta S^\ddagger = 9.14 \text{ e. u.}$$

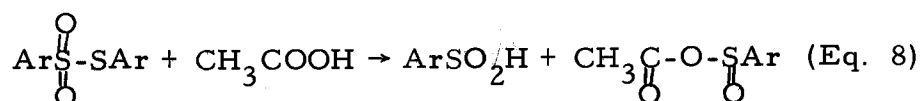
good first-order kinetics and a half-life of about 25 minutes at 50° C. In the presence of various amounts of added p-toluenesulfinic acid the decomposition retains its strict first-order nature. In addition to the first-order character being unaffected, the rate of the decomposition of II is totally unaffected by any concentration of added p-toluenesulfinic acid. The amounts of added p-toluenesulfinic acid varied from slightly less than one molar equivalent to slightly greater than two molar equivalents of the sulfinic acid per mole of II. These results are shown in Tables I and II.

Effect of Solvent on the Rate of Decomposition
of p-Toluenesulfinyl p-Tolyl Sulfone

The rate of decomposition of p-toluenesulfinyl p-tolyl sulfone was measured in anhydrous dioxane, anhydrous acetonitrile, and acetic acid. The results are also shown in Tables I, II, and III. The rate in each of these three solvents is about the same. However, the entropy and enthalpy of activation do show a change, with the change in one essentially compensating for the change in the other. For p-toluenesulfinyl p-tolyl sulfone in dioxane, dielectric constant equal to 2.05 (1), the enthalpy of activation is 27.8 kilocalories per mole and the entropy of activation is 11.7 calories per degree per mole, whereas in acetonitrile, dielectric constant equal to 37.45 (77), the enthalpy and entropy of activation are 25.7 kilocalories per mole

and 5.5 calories per degree per mole.

In acetic acid the results are roughly the same. However, in these runs there was always a large residual concentration of sulfinic acid, which suggested that some of the sulfinyl sulfone had undergone solvolysis, possibly via a process such as Eq. 8. This large amount of residual sulfinic acid also tends to disproportionate fairly rapidly,



which further complicates interpretation of the rate data in this solvent. The apparent enthalpy and entropy of activation in acetic acid are 28.2 kilocalories per mole and 9.14 calories per degree per mole, but there is obviously considerable question about their real accuracy.

Products of the Decomposition of p-Toluenesulfinyl p-Tolyl Sulfone

The products of the decomposition of p-toluenesulfinyl p-tolyl sulfone, II, were investigated in the following manner: A known amount of II was diluted to a known volume with anhydrous solvent. It was decomposed in a manner identical with that used for the kinetics, with several aliquots taken during the decomposition to insure that the rate was normal. At the end of the decomposition an aliquot was removed, added to 1.5 N sulfuric acid, as in the procedure for

the kinetics, and titrated with 0.200 N sodium nitrite to determine the amount of residual sulfinic acid. Another aliquot was removed, water was slowly added to it in large excess, and the mixture was titrated with 0.100 N sodium hydroxide to the bromothymol blue end point. This determines the total amount of titratable acid. This will include *p*-toluenesulfonic acid formed from the decomposition and any residual sulfinic acid. Another aliquot was added directly to anhydrous ether. The anhydrous ether was quickly given two washings with water and this water layer titrated with 0.1 N sodium hydroxide to the bromothymol blue end point. Control experiments proved that by this procedure sulfonic acid anhydrides remain completely in the ether layer and are not notably hydrolyzed by the washing of the ether layer with water, whereas any sulfonic acid present is transferred completely to the water layer.

A large volume of water was added to the remainder of the reaction solution from the decomposition of II. The mixture was extracted with ether several times and the ether fractions were washed with water, dried, and the ether removed under reduced pressure. These ether soluble products were then separated by chromatography on acid-washed alumina. The water-soluble products were isolated by removing the water under reduced pressure.

Products in the Absence of Added Sulfinic Acid. In the absence of added sulfinic acid, *p*-toluenesulfinyl *p*-tolyl sulfone decomposes

to p-toluenesulfonic acid, p-tolyl p-toluenethiolsulfonate, and di-p-tolyl disulfide. These results are shown in Table IV.

The yield of p-toluenesulfonic acid is about 0.9 mole per mole of II. In dioxane, less than one percent of this acid is in the form of its anhydride, whereas in acetonitrile about 30 percent is found to exist as its anhydride. The p-toluenesulfonic acid was identified by melting point and infrared of both itself and its p-toluidine salt.

The p-tolyl p-toluenethiolsulfonate and di-p-tolyl disulfide from the ether fraction were identified by melting point, infrared spectrum and mixed melting point with known samples. Their exact yields varied depending upon the dryness of the system, with the yield of the disulfide increasing and that of the thiolsulfonate decreasing as precautions were taken to keep the system anhydrous. The driest system obtained was where the glassware was flamed dry while being swept out with anhydrous nitrogen. Connected to this apparatus was a distillation apparatus from which dioxane was distilled. The dioxane was distilled directly from the sodium ketyl of benzophenone (79). Under these rigorously anhydrous conditions the yield of p-tolyl p-toluenethiosulfonate was 0.17 mole per mole of II and that of the disulfide was 0.25 mole per mole of II.

Early during the decomposition in dioxane, the solution turns a light yellow color, which persists throughout the decomposition. This color is immediately discharged upon the addition of water or

Table IV. Products of the Decomposition of p-Toluenesulfinyl p-Tolyl Sulfone.

Concentration of Reactants:	Dioxane	Dioxane	Dioxane	Acetonitrile
p-Toluenesulfinyl p-Tolyl Sulfone, M	0.050	0.043	0.042	0.051
p-Toluenesulfinic Acid, M	0.000	0.042	0.086	0.000
Products, expressed in moles/mole of II decomposed:				
p-Tolyl p-Toluenethiolsulfonate	0.17	0.93	0.96	0.55
di-p-Tolyl Disulfide	0.25	0.00	0.00	trace
p-Toluenesulfonic Acid ^{1/}	0.89	0.94	0.93	0.83 ^{3/}
Residual p-Toluenesulfinic Acid	0.00	0.13	1.15	0.00
Moles p-Toluenesulfinic Acid Consumed/mole II		.86	0.89 ^{2/}	

^{1/} This sulfonic acid is the total acid titrated with .1 N NaOH to bromothymol blue end point less the sulfinic acid determined by titration with NaNO₂.

^{2/} Not corrected for small amount of disproportionation.

^{3/} 30% of this acid as sulfonic anhydride.

sulfinic acid. Whether water or sulfinic acid is added to discharge this color has only a small effect on the proportions of the products, the yield of the thiolsulfonate being slightly increased and the yield of the disulfide being proportionately decreased if sulfinic acid is added instead of water.

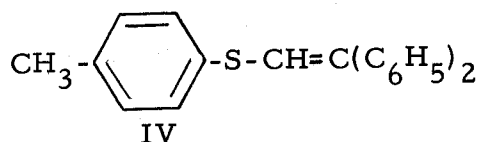
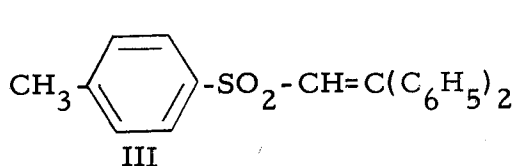
In acetonitrile the yield of p-toluenesulfonic acid is about the same as in dioxane; however, as mentioned, about 30 percent of this acid is in the form of its anhydride. The yield p-tolyl p-toluenethiolsulfonate is increased to 0.55 mole per mole of decomposed II. The yield of di-p-tolyl disulfide is decreased to traces. However, it is not certain that the acetonitrile studies were carried out under anywhere near as truly anhydrous conditions as the product studies in dioxane.

Products in the Presence of Added Sulfinic Acid. In the presence of p-toluenesulfinic acid the products from the decomposition of p-toluenesulfinyl p-tolyl sulfone are markedly different. Although the presence of the added sulfinic acid does not affect the rate or the first-order kinetics, about 0.89 mole of p-toluenesulfinic acid is consumed per mole of II decomposed. The yield of p-tolyl p-toluenethiolsulfonate is approximately the same as that of the sulfonic acid, 0.95 mole per mole of II. No di-p-tolyl disulfide was formed when II was decomposed in the presence of added sulfinic acid.

These results are also shown in Table IV.

Decomposition of p-Toluenesulfinyl p-Tolyl Sulfone in the Presence of Added Olefin

The rate of decomposition of p-toluenesulfinyl p-tolyl-sulfone was unaffected by the presence of added 1, 1-diphenylethylene. However, once again the products were markedly different. The yield of p-tolyl p-toluenethiolsulfonate was 0.23 mole per mole of sulfinyl sulfone. More important two new products were formed, 0.20 mole p-tolyl 2, 2-diphenylvinyl sulfone, III, and 0.18 mole p-tolyl 2, 2-diphenylvinyl sulfide, IV, per mole of II. Because of the large amount of 1, 1 diphenylethylene used in these experiments, 1.7 M, any di-p-tolyl disulfide formed could not be separated from the large amount

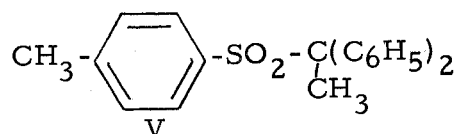


of unreacted olefin which was recovered. Separation of these products was effected by chromatography on alumina. In addition, traces of unidentifiable oils were also obtained from the chromatography.

One must demonstrate that III and IV do not arise from some reaction between the products from the decomposition of II and 1, 1-diphenylethylene. p-Toluenesulfonic acid, p-tolyl p-toluenethiolsulfonate, and 1, 1-diphenylethylene were mixed together in dioxane and subjected to the identical conditions used for the decomposition

of II. Upon analysis of this mixture, all that could be found were the starting materials in their original form. Therefore, no reaction takes place between 1,1-diphenylethylene and the products from the decomposition of II.

It is also important to demonstrate that III could not arise from a reaction between p-toluenesulfonic acid, which might somehow be formed in the course of the reaction, and 1,1-diphenylethylene. This was accomplished by dissolving p-toluenesulfonic acid, p-toluenesulfonic acid, and 1,1-diphenylethylene together in dioxane and subjecting this solution to the identical conditions used for the decomposition of II. No III was formed. However, a new compound was isolated, p-tolyl 1,1-diphenylethyl sulfone, V.



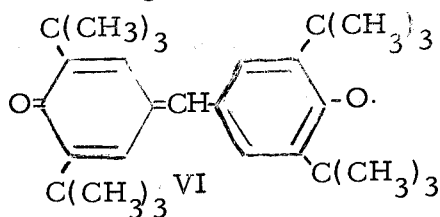
p-Toluenesulfinyl p-tolyl sulfone was also decomposed in the presence of methyl methacrylate in an attempt to initiate polymerization of the olefin. When II was decomposed in a dioxane solution containing methyl methacrylate 60 times as concentrated as II, no polymer of sufficient molecular weight to cause it to be insoluble in methanol was produced. The temperatures at which these experiments were carried out were varied from 30° to 65° C. to vary any polymerization initiation rates which might be taking place. The

results, however, were unaffected. Although no polymer was produced, which could be precipitated by methanol, it was noted that the dioxane solution of methyl methacrylate did increase in viscosity during the decomposition of II.

Azobis-isobutyronitrile under the same conditions produced a sizeable quantity of polymerized methyl methacrylate. But, when azobis-isobutyronitrile and II were decomposed together in a dioxane solution of methyl methacrylate no polymer was produced.

The Thermal Decomposition of p-Toluenesulfinyl p-Tolyl Sulfone in the Presence of Galvinoxyl

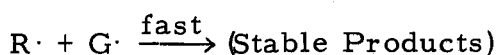
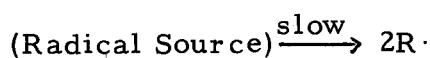
The stable free radical galvinoxyl, 2,6-di-tert-butyl-(3,5-di-tert-butyl-4-oxo-2,5-cyclohexadiene-1-ylidene)-p-tolyloxy, VI, has been successfully used to scavenge and intercept short-lived free



radicals (6). The reaction between galvinoxyl and other radicals is extremely rapid. Therefore, the rate of disappearance of galvinoxyl is controlled by the rate of production and diffusion of the radicals to be intercepted. The concentration of this deep blue radical can be followed over a range from 10^{-3} to 10^{-4} M by use of a shoulder in its visible spectrum at 530 millimicrons ($\epsilon = 560$). These low concentrations allow one to follow the decrease in optical density

directly on the reaction solution without diluting. In the present work all of the reactions using galvinoxyl were carried out in a standard Beckman Pyrex cell in a spectrophotometer thermostated at 29.3°.

It is advantageous to keep the concentration of the radical-producing source ten to 100 times greater than the initial concentration of galvinoxyl. Under these conditions, the fraction of the radical source which needs to decompose in order to consume all of the galvinoxyl is small, and the concentration of the radical-producing source and the rate of radical production will remain effectively constant throughout the course of the experiment. Since the production of trappable radicals is the rate-determining step in the consumption of galvinoxyl, and since this rate will remain constant during



$\text{R}\cdot$ = Free Radical

$\text{G}\cdot$ = Galvinoxyl

the experiment, the galvinoxyl should disappear by zero-order kinetics. The efficiency with which the free radical source yields trappable free radicals will be the zero-order rate of consumption of galvinoxyl divided by the rate of decomposition of the source. In the case of II, the rate of decomposition will be the first-order rate constant times the concentration of II times two, since for each molecule of II which decomposes by a radical mechanism two

$$\text{Efficiency} = k_o / 2k_1(\text{II})$$

k_o = Zero-order Rate for Galvinoxyl Consumption

k_1 = Rate of Decomposition of II

(II) = Initial Concentration of II

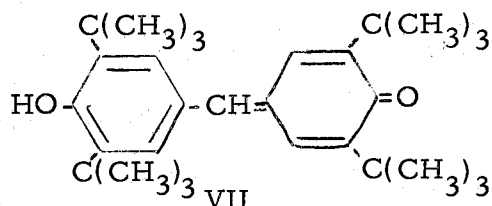
radicals will be produced.

p-Toluenesulfonic acid and p-tolyl p-toluenethiolsulfonate were found not to react at an appreciable rate with galvinoxyl in dioxane. However, galvinoxyl does react with excess p-toluenesulfonic acid via a reaction which is first-order in galvinoxyl. Doubling the p-toluenesulfonic acid concentration doubles the pseudo first-order rate constant for the disappearance of galvinoxyl indicating that this reaction is also first-order in sulfinic acid.

Since galvinoxyl reacts with sulfinic acid it is necessary to remove any traces of sulfinic acid from II before attempting to count radical production from II with galvinoxyl. To do this, II was dissolved in a small volume of anhydrous benzene and chromatographed on a column of 50 percent anhydrous magnesium sulfate and 50 percent dried Celite. The elution of II from the column was followed by use of an ultra-violet light. After eluting with 25 milliliters of benzene the main fraction of II was collected in a fraction of about 25 milliliters volume and the solvent was evaporated under vacuum at a temperature slightly below room temperature. The residual sulfinyl sulfone was dried at room temperature under 0.1

millimeter vacuum for one hour and then used immediately. From hydrolysis of a weighed portion of this chromatographed II and then titration with 0.1 N sodium nitrite, it was found that about 35 percent had decomposed during this treatment.

In the presence of II treated in this manner galvinoxyl disappeared by a process that was zero-order in galvinoxyl. From the initial zero-order rate constant it is calculated that about 44 percent of the sulfinyl sulfone decomposing yields radicals trapped by galvinoxyl. These results are shown in Table V. The initial zero-order rate was used in calculating the efficiencies because in the latter stages the rate of fading of galvinoxyl decreases somewhat. There are two probable sources for this retardation. First, dissociation of the sulfinyl sulfone-galvinoxyl products would retard the fading of the solution's optical density by adding galvinoxyl back to the solution. Second, it has been reported (36) that hydrogalvinoxyl, VII, exists as an inherent impurity in galvinoxyl solutions. In the



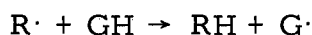
present work it was found that a solution of II and hydrogalvinoxyl underwent an increase in optical density at a rate of about one-tenth the rate for the disappearance of galvinoxyl under the same conditions as shown in table V. Undoubtedly, this optical density increase

Table V. Decomposition of p-Toluenesulfinyl p-Tolyl Sulfone in the Presence of Galvinoxyl in Dioxane at 29.3°.

$(\text{II}) \times 10^2 \text{ } \underline{1/}$ M	$(\text{Galvinoxyl}) \times 10^3$ M	$k_o \times 10^7$ M sec. ⁻¹	$k_o / 2k_1 (\text{II})_o \text{ } \underline{2/}$
0.8	0.8	1.73	0.51
1.9	0.8	3.3	0.41
3.5	0.8	5.9	0.40
1.2	1.75	2.5	0.48
0.5	1.95	0.87	<u>0.40</u>
		Average	0.44

1/ Sulfinyl Sulfone purified by chromatography; these initial concentrations are corrected for 35% decomposition of II during chromatography.

2/ k_1 is the first-order rate constant for the decomposition of II in dioxane at 29.3° C.



R = Free Radical

GH = Hydrogalvinoxyl

G· = Galvinoxyl

is due to the radicals from the decomposition of II abstracting a hydrogen from hydrogalvinoxyl to form galvinoxyl. This optical density increase leveled off sharply at a galvinoxyl to hydrogalvinoxyl ratio of one to five.

Influence of Sulfinyl Sulfone Structure on Rate of Decomposition

The variation in rate of decomposition of several arenesulfinyl aryl sulfones with structure of the aryl group was measured in dioxane using the same procedure as was used for II. All of the sulfinyl sulfones studied followed good first-order kinetics, decomposing in a manner very similar to that of II. Variation of aryl group causes only a small change in the rate of decomposition. These results are shown in Table VI. A plot of the logarithm of the first-order rate constant for the p-tolyl, p-chlorophenyl, and phenyl compounds against the Hammett sigma constant shows a positive slope of 0.67, indicating that electron-withdrawing substituents in the aromatic ring tend to accelerate the rate of decomposition. The enthalpy and entropy of activation for the p-chlorophenyl compound are 28.4

Table VI. Influence of Sulfinyl Sulfone Structure on Rate of Decomposition in Dioxane.

Sulfinyl Sulfone	Temp. °C	(ArSO ₂ SOAr) M	$k_1 \times 10^4$ sec. ⁻¹
Phenyl	49.3	0.05	4.45
		0.075	5.10
		0.05	4.79
		0.1	4.79
β-Naphthyl	49.3	0.053	5.2
		0.044	6.3
		0.059	6.2
		0.039	6.0
p-Chlorophenyl	49.3	0.05	6.40
		0.05	6.40
	39.5	0.05	1.40
		0.05	1.40
	29.4	0.05	0.34
		0.05	0.32

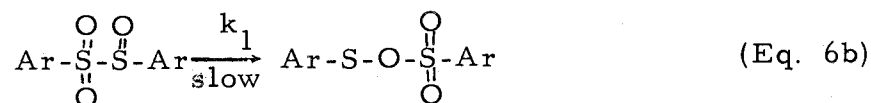
$$\Delta H^\ddagger = 28.4 \text{ Kcal./mole}$$

$$\Delta S^\ddagger = 14.3 \text{ e. u.}$$

kilocalories per mole and 14.3 calories per degree per mole.

Attempted Preparation of a Sulfenyl Sulfonate

Kice and Bowers (42) in their investigation of the disproportionation of p-toluenesulfinic acid suggested that the proposed intermediate, II, might decompose by a rearrangement to a mixed sulfonic-sulfenic anhydride (Eq. 6b). Considering the data collected on sulfinyl sulfones, this is still, indeed, an attractive mechanism. Therefore, it seemed interesting and useful to attempt to prepare



a sulfenyl sulfonate.

2,4-Dinitrobenzensulfenyl chloride was mixed under a dry nitrogen atmosphere with silver p-toluenesulfonate in anhydrous acetonitrile at 0°C. The silver chloride which precipitated was filtered off and di-2,4-dinitrophenyl disulfide immediately started precipitating slowly from the solution. The disulfide was filtered off and the solvent distilled off at reduced pressure to yield an insoluble yellow tar.

The above preparation was repeated in the same manner except the sulfenyl chloride was dissolved in ether and to this was added the powdered silver sulfonate. The results were the same.

The first preparation was repeated again in the same manner,

except that this time when the silver chloride was filtered off, the filtrate was run directly into ice water. A yellow oil separated. When this oil was either touched by a glass rod, touched by sodium chloride infrared cells, or put into chloroform for an infrared spectrum, it turned to yellow tar.

The above experiments were repeated using p-toluenesulfonyl chloride in place of the 2,4-dinitrobenzenesulfonyl chloride. The results were the same.

It was impossible to measure quantitatively the yield of the products from the sulfonyl sulfonate decomposition due to the insolubility of di-2,4-dinitrophenyl disulfide which precipitated with the silver chloride, and the insolubility of the yellow tars. However, the yield of the disulfide and the sulfonic acid was considerable. From the infrared spectrum of the yellow tar it can be seen that some thiolsulfonate was also present. When chromatography of this tar was attempted, yellow oil washed off the column with the thiol-sulfonate.

DISCUSSION

Kinetics of the Decomposition of II

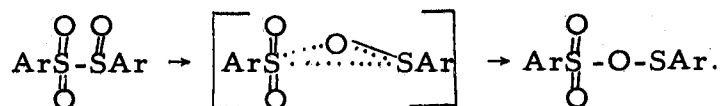
The strict first-order kinetics for the decomposition of sulfinyl sulfones strongly suggests a rate-determining unimolecular decomposition. Since neither the rate nor the order of the decomposition is affected by the presence of various concentrations of added sulfinic acid, there is no direct reaction between sulfinyl sulfone and sulfinic acid of the type suggested by Bredereck and co-workers (7, 12, 13).

However, the drastic alteration of the proportions and the nature of the products of the decomposition of II in the presence of added p-toluenesulfinic acid shows that, while sulfinic acid does not react directly with II, it does react with intermediates formed by the decomposition of II. Although, added p-toluenesulfinic acid has no kinetic influence on the decomposition of II, nearly one mole of the sulfinic acid is consumed per mole of II decomposed. These various results can be accounted for by a rate-determining unimolecular decomposition of II into reactive intermediates, which then react rapidly with any sulfinic acid present. Such a scheme is, of course, of exactly the type suggested by Kice and Bowers (42) in order to explain their kinetic results on the disproportionation of

sulfinic acids (see p. 7, eq. 6). The present study of the sulfinyl sulfone decomposition thus rules out Brederick's idea of a direct reaction between II and sulfinic acid (Eq. 5e) and provides strong support for the Kice and Bowers mechanism for the disproportionation of sulfinic acids (Eq. 6).

Evidence that the Sulfinyl Sulfone Decomposition Involves a Homolytic Scission of the Sulfur-Sulfur Bond

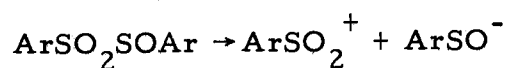
Given the fact that the rate-determining step in the decomposition of the sulfinyl sulfone is a unimolecular reaction, exactly what kind of a reaction is it? Something can be inferred about its nature from the effect on the rate of changes in solvent and from the magnitude of the activation parameters in different solvents. In dioxane the enthalpy and entropy of activation for the decomposition of II are 27.8 kilocalories per mole and 11.7 e. u. respectively. The rather large positive entropy of activation suggests that the reaction does not involve a concerted cyclic rearrangement directly to the sulfonyl sulfonate, such as:



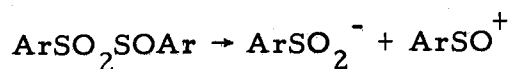
For a process of this type one would expect the entropy to be much more negative.

A change in solvent from dioxane to acetonitrile does not lead

to any large change in the rate of decomposition. Acetonitrile, dielectric constant equal to 37.45, is undoubtedly a more powerful ionizing solvent than dioxane, dielectric constant equal to 2.05. Therefore, if the decomposition of II involved a rate-determining heterolytic dissociation of the sulfur-sulfur bond into a pair of oppositely charged ions, the rate would undoubtedly be greatly



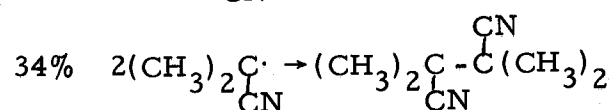
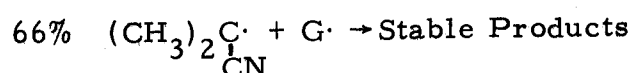
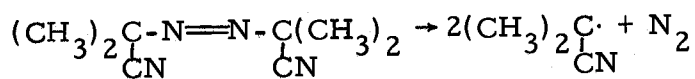
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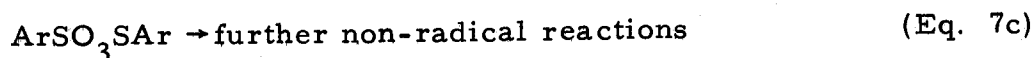
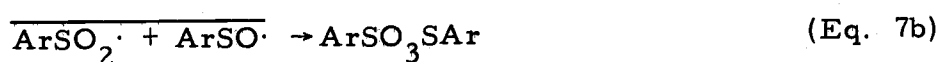
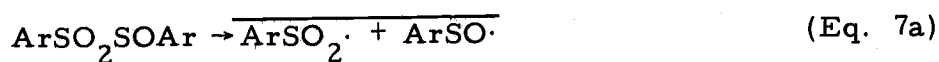
enhanced upon going from dioxane to acetonitrile. Since a large change in solvent ionizing power does not lead to any significant change in rate of decomposition, the rate-determining step of the sulfinyl sulfone decomposition does not appear to involve any such heterolytic dissociation. Therefore, since we previously ruled out a concerted cyclic mechanism, a homolytic scission of the sulfur-sulfur bond into a pair of free radicals seems the most likely possibility. We must next consider whether there is any additional evidence strongly indicating the likelihood of a radical mechanism. Before doing this we should note, however, that the enthalpy and entropy of activation for the decomposition of p-chlorobenzenesulfinyl p-chlorophenyl sulfone in dioxane, 28.4 kilocalories per mole and 14.3 e. u., are very similar to those for II. This shows that both of these compounds presumably decompose by the same mechanism.

In any system the best evidence for a radical decomposition is supplied by successful efforts to detect and trap the radicals formed. In the present work positive evidence for the presence of radical intermediates was obtained in two separate types of experiments, and a result suggestive of radicals was obtained in a third.

Studies with the stable free radical galvinoxyl leave little doubt that II decomposes by a homolytic scission of the sulfur-sulfur bond into free radicals. The apparent efficiency of trapping by galvinoxyl, 44 percent, can be compared with the 66 percent efficiency of galvinoxyl in trapping radicals from the decomposition of azo-isobutyronitrile (6). The 34 percent radicals from the decomposition of azo-isobutyronitrile which are not trapped by galvinoxyl are



consumed by cage recombination to stable products. It is very likely that the major portion of the radicals formed from the decomposition of II undergo recombination while still within the



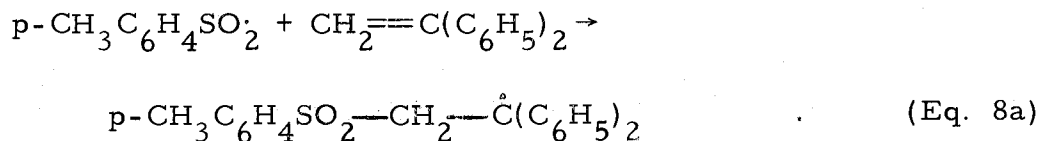
solvent cage to form an intermediate which undergoes further

product-forming reactions by non-radical mechanisms (Eqs. 7).

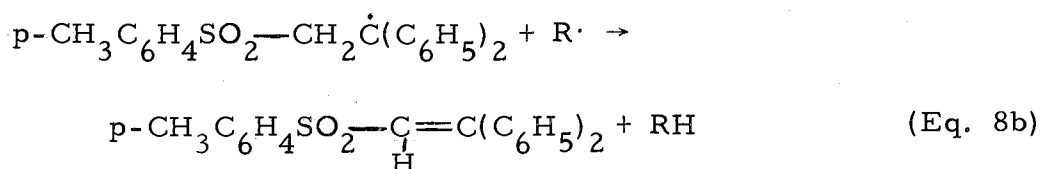
Any radicals reacting in this fashion are not detected by galvinoxyl.

A reasonable choice for this new intermediate is the sulfenyl sulfonate previously suggested by Kice and Bowers (42).

Decomposing II in the presence of an olefin susceptible to radical attack but sterically hindered against polymerization should lead to stable, isolable radical-olefin reaction products. This was found to be the situation in the present work, using diphenylethylene as the olefin. The formation of the sulfone, III, from the decomposition of II in the presence of diphenylethylene can be accounted for by a sequence such as Eq. 8. In this scheme, the radical



VIII



III

intermediate VIII would be expected to be a well stabilized and relatively unreactive radical. In addition, the carbon bearing the free radical is sterically hindered. Thus, it is not surprising that VIII does not couple with a second radical or abstract a hydrogen atom from a solvent molecule but, rather, undergoes termination by

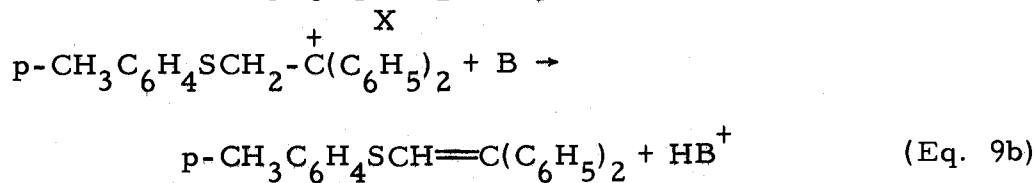
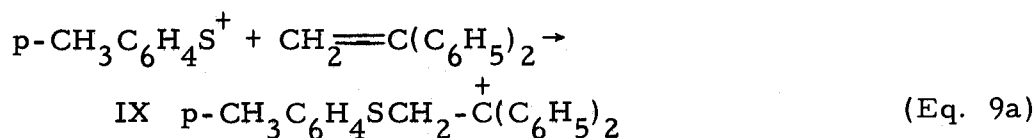
transfer of a β -hydrogen to another radical in the solution. The radical, $R\cdot$, could be either a radical derived from the solvent by abstraction of a solvent hydrogen by one of the radicals from the decomposition of II, or it could be one of the radicals formed directly by the decomposition of II.

The only alternative route to III would be an initial addition of $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2^+$ to the olefin followed by loss of a proton from the carbon atom adjacent to the resulting carbonium ion. This route seems quite unlikely since there are indications (51) that sulfonylium ions, ArSO_2^+ , are very highly unstable species which are formed only under very forcing conditions. It does not seem likely that a sulfonylium ion would be formed under the mild conditions used in the present work.

In addition, there are the effects of solvent on the rate of decomposition of II, which argue against a scission of II into ions, and the galvinoxyl studies, which strongly suggest that II decomposes by a radical mechanism. The weight of the evidence therefore seems to suggest that III arises via a free radical process.

The sulfide, IV, also found in the decomposition in the presence of diphenylethylene, most likely arises via an ionic process (Eqs. 9) in which the sulfenium ion, IX, adds to the olefin to give a carbonium ion, X, which then loses a proton to form the product IV. The isolation of IV is good evidence that sulfenium ions exist in the

decomposition solution of II and thereby supports the previous

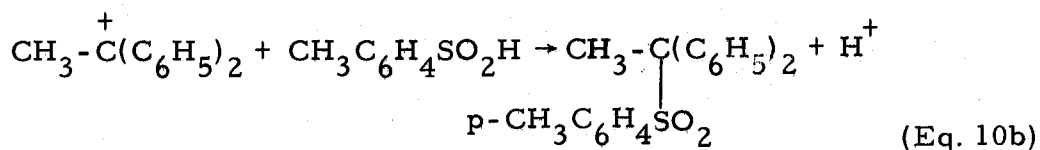
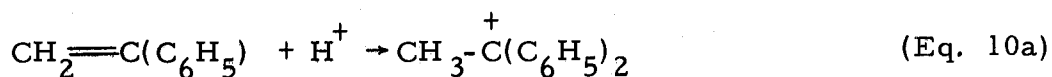


IV

suggestion that II decomposes into radicals which undergo considerable recombination in the solvent cage to form a sulfenyl sulfonate.

Recent work by Pettitt and Helmkamp (67) demonstrates that although sulfenyl sulfonates cannot be isolated, they behave in solution as sulfenium and sulfonate ions and will add to olefins similarly to sulfenyl halides (38, p. 382-384).

The sulfone, V, formed from p-toluenesulfonic acid, p-toluenesulfinic acid and 1,1-diphenylethylene most likely arises via an acid catalyzed addition of sulfinic acid to the olefin (Eqs. 10).



V

A well known and much exploited method of counting free radicals is the polymerization of olefins such as methyl methacrylate.

The free radical propagation and termination rates are known for this olefin. Therefore, by isolating and weighing the polymer formed in the presence of a radical source one can calculate the initiation rate.

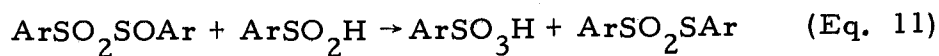
Decomposition of II in the presence of methyl methacrylate failed to produce polymer but it was noted that the solution did increase in viscosity. This could mean that 1) there is an inhibitor present as an impurity in II, 2) II itself acts as an inhibitor, 3) the initiation rates by II are so large that the propagating chains are short and the polymer is not of high enough molecular weight to be precipitated by methanol, or finally, 4) II does not decompose by a homolytic cleavage into radicals.

Azo-isobutyronitrile, a known initiator, and II were decomposed together in a solution of methyl methacrylate in dioxane. Dumping the decomposed solution into methanol failed to precipitate any polymer. Therefore, either there is an inhibitor present or the initiation rate is so large that the propagating chains are too short to be precipitated by methanol.

Products from the Sulfinyl Sulfone Decomposition

The products from the decomposition of II in the presence of added sulfinic acid are in accord with those reported by Bredereck and co-workers (7, p. 63; 11, 12), although in the present work the

yield of thiolsulfonate was found to be close to 95 percent of that expected from Eq. 11, considerably larger than that reported earlier.



A recent investigation in these laboratories¹ on the rate of hydrolysis of II indicates that in the absence of strong acid and in the presence of small concentrations of water, the hydrolysis of II is probably not rapid enough to compete significantly with its thermal decomposition.

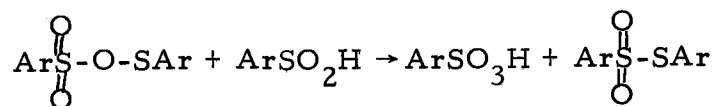
Yet, in the present work it was observed that the presence of moisture had a profound effect upon the proportions of the products formed in the thermal decomposition of II. Specifically, when the reaction system was kept rigorously anhydrous by flushing the apparatus with anhydrous nitrogen while flaming the glassware with a Bunsen burner and then distilling the dioxane from the sodium ketyl of benzophenone directly into the reaction vessel, decomposition of II in the presence of one molar equivalent of p-toluenesulfonic acid led to the formation of 0.95 mole of thiolsulfonate per mole of II and the consumption of 0.87 mole of p-toluenesulfonic acid per mole of II. However, if the dioxane was distilled in the same manner but the solution was then exposed to the atmosphere briefly while transferring it into the reaction vessel, the yield of thiolsulfonate was

¹Venier, Clifford G. Unpublished Research. Oregon State University, Corvallis, Oregon. 1965.

somewhat lower and the consumption of p-toluenesulfinic acid per mole of II decomposed was much less.

It appears then, that very small amounts of moisture can play an important role in the product forming reactions which follow the unimolecular decomposition of II.

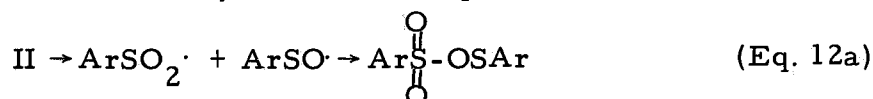
The work of Pettitt and Helmkamp (67) and the present work both strongly indicate that sulfenyl sulfonates are extremely sensitive to moisture. Also, Pettitt and Helmkamp's (67) work gives evidence that sulfenyl sulfonates behave very similarly to sulfenyl halides. It is known (75) that sulfenyl halides react very readily with sulfinic acids to form the corresponding thiolsulfonate and halogen acid. It therefore seems likely that both water and sulfinic acid would react rapidly with any sulfenyl sulfonate formed during the decomposition of II and that the pronounced influence of small amounts of moisture is due to its altering the course of the reaction by reacting with the sulfenyl sulfonate, which would otherwise react with sulfinic acid according to the following equation:



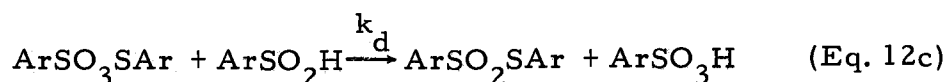
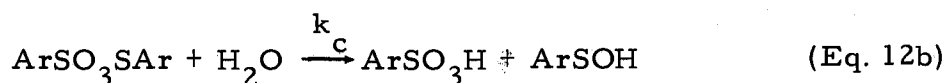
Just how the reaction with water might lead to a somewhat decreased yield of thiolsulfonate and a much decreased consumption of sulfinic acid will be outlined shortly.

We have already seen that the available evidence suggests that

the thermal decomposition of a sulfinyl sulfone involves an initial homolytic scission of the sulfur-sulfur bond, giving an $\text{ArSO}_2\cdot$ and an $\text{ArSO}\cdot$ radical. These radicals can then recombine in a head-to-tail fashion to give the sulfenyl sulfonate (Eq. 12a).

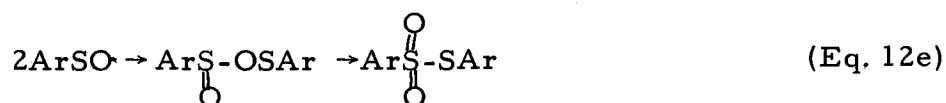
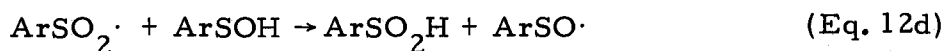


One explanation for the pronounced effect which water has on the stoichiometry of the decomposition is the following: Water, being a better nucleophile, reacts more rapidly with the sulfenyl sulfonate than does the sulfinic acid (Eq. 12b, c). If one were then to have a



$$k_c > k_d$$

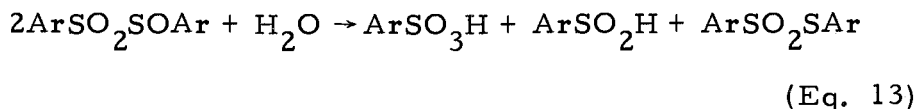
rapid hydrogen atom transfer reaction involving the sulfinic acid, ArSOH , and an $\text{ArSO}_2\cdot$ radical followed by combination of $\text{ArSO}\cdot$ radicals (Eq. 12d, e) one could explain the changes in stoichiometry



brought on by the presence of small amounts of moisture. Incidentally, the work of Topping and Kharasch (78) suggests that the $\text{ArSO}\cdot$ radicals undergo coupling which leads to near-quantitative yields of

thiolsulfonate (Eq. 12e).

Summation of the stoichiometry represented by Eqs. 12a, b, d, e gives Eq. 13.



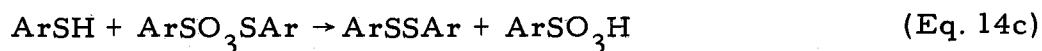
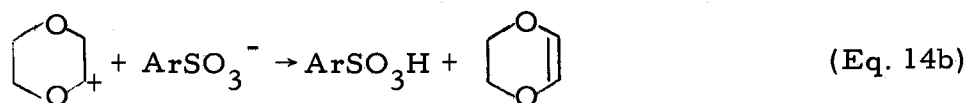
On the other hand, in the absence of moisture the sulfenyl sulfonate reacts only with sulfinic acid (Eq. 12c) and the over-all stoichiometry is as shown in Eq. 11.

Both Eqs. 11 and 13 predict that a given decomposition should produce the same amount of sulfonic acid as it does of thiolsulfonate. Within experimental error such was always observed to be the case in the various decompositions of II in the presence of sulfinic acid. On the other hand the total yield of either will be less when any moisture is present and the amount of sulfinic acid consumed will be less since that fraction of II which is consumed via the stoichiometry of Eq. 13 actually leads to sulfinic acid as one of the products.

In the present work, as has also been found by Pettitt and Helmkamp (67), sulfenyl sulfonates were found to be too unstable to isolate or purify. One of their principal decomposition products in the absence of a nucleophile such as water or sulfinic acid seems to be the disulfide. It was also observed that the dioxane solution from the decomposition of II in the absence of added sulfinic acid turned a light yellow color. This color was immediately discharged upon the

addition of water or p-toluenesulfonic acid. Whether water or sulfonic acid was added had a small effect on the proportions of the products. Since aromatic sulfenyl compounds often give yellow dilute solutions, it seems very likely that the yellow color observed in the present work is due to a small build-up of the sulfenyl sulfonate. In the absence of sulfonic acid and moisture this sulfenyl sulfonate decomposes to the disulfide and sulfonic acid.

There is no evidence to allow one to say exactly how the disulfide and sulfonic acid are formed from the decomposition of sulfenyl sulfonate, but the possibility that dioxane plays a role is suggested by the report that sulfenyl chlorides attack ethers (38, p. 387). Coupled with this is the isolation of traces of unidentified oils from the decomposition solution, one of which contains an aldehyde function. A possible role for this utilization of solvent in the decomposition is depicted in Eq. 14. In this scheme dioxane



serves to reduce the sulfenium ion to a mercaptan (Eq. 14a) and also to furnish protons for the sulfonic acid (Eq. 14b). Since mercaptans

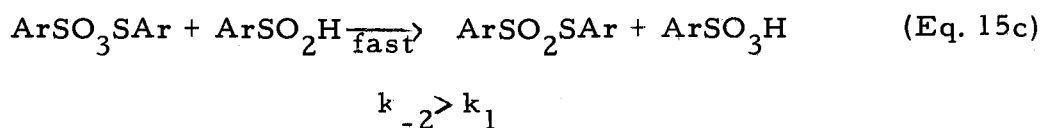
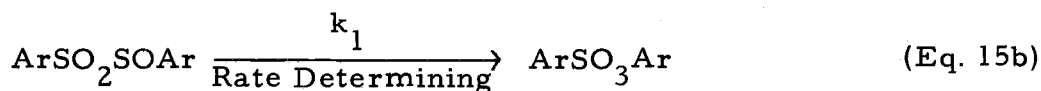
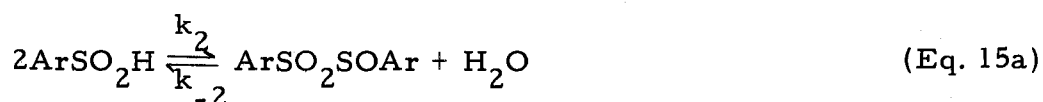
are known to react rapidly with sulfenyl halides to form disulfides (38, p. 390) any mercaptan formed would undoubtedly react very rapidly with some of the remaining sulfenyl sulfonate to give the disulfide (Eq. 14c).

There are several possible routes by which thiolsulfonate may be formed during the decomposition of II in the absence of added sulfinic acid. First, any traces of moisture would lead to the formation of thiolsulfonate and sulfinic acid via Eq. 13, and the sulfinic acid would then react with additional sulfenyl sulfonate as shown in Eq. 12c. Second, an $\text{ArSO}_2\cdot$ radical could abstract a hydrogen atom from a solvent molecule thereby yielding some of the corresponding sulfinic acid. This sulfinic acid would then also react with sulfenyl sulfonate to form sulfonic acid and thiolsulfonate (Eq. 12c). Third, any termination involving a pair of $\text{ArSO}\cdot$ radicals (Eq. 12e) would, as already mentioned, be expected to form the thiolsulfonate.

Evidence Which Indicates that Sulfinyl Sulfones
are Involved in the Disproportionation of Sulfinic Acids

Kice and co-workers (42, 45) found the disproportionation of sulfinic acids to be second-order in sulfinic acid. This means that the rate-determining transition state is derived from two molecules of sulfinic acid. The disproportionation is strongly retarded by water and is only slightly enhanced by added mineral acid. Since the

reaction is only moderately catalyzed by added strong acid, it is not likely that the water retards it by moderating the acidity of the medium. The retardation of the rate by added water could, however, be easily explained by a mechanism such as that shown in Eq. 15, in which an initial equilibrium between sulfinic acid and the sulfinyl sulfone is followed by rate-determining thermal decomposition of the sulfinyl sulfone. With the present knowledge about the behavior of sulfinyl sulfones and their thermal decomposition the sulfinyl sulfone is indeed an excellent choice as the intermediate through which sulfinic acids disproportionate. The mechanism represented in Eq. 15 fits the above data quite well and has the added virtues of being plausible and simple.



Kice and co-workers (45) report that the rate of disproportionation of p-substituted benzenesulfinic acids is retarded by electron-withdrawing groups while electron-releasing p-substituents accelerate the rate of disproportionation. In the present work it was observed that the same substituents produced the opposite effect in

the corresponding sulfinyl sulfone. Aromatic sulfinyl sulfones with electron-withdrawing p-substituents decompose more rapidly than those with electron-releasing p-substituents. This means that the effect of substituents on the rate of disproportionation must be the result of their influence on the initial equilibrium between the sulfinic acid and the sulfinyl sulfone (Eq. 15a). In the sulfinyl sulfones there is a repulsion between the two adjacent, electron-deficient sulfur atoms. Figure I represents this repulsion in terms of formal charge (28). Electron-withdrawing substituents would enhance the

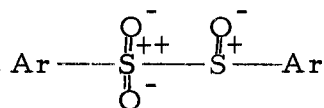


Figure I

magnitude of this repulsion thus increasing the free energy of the sulfinyl sulfone. Eq. 16 shows that an increase in the free energy difference between sulfinic acid and sulfinyl sulfone will decrease the initial equilibrium constant, K . In Eq. 16b the concentrations

$$\Delta F = -RT \ln K \quad (\text{Eq. 16a})$$

$$K = \frac{(\text{ArSO}_2\text{SOAr})(\text{H}_2\text{O})}{(\text{ArSO}_2\text{H})^2} \quad (\text{Eq. 16b})$$

of the compounds expressed in the parentheses are expressed as their activities. The observed rate constant, k_{obs} , for the disproportionation of sulfinic acids, contains both the sulfinic

acid-sulfinyl sulfone equilibrium constant and the decomposition rate constant for the sulfinyl sulfone (Eqs. 17). Electron-withdrawing substituents cause a slight increase in k_1 , but this increase is

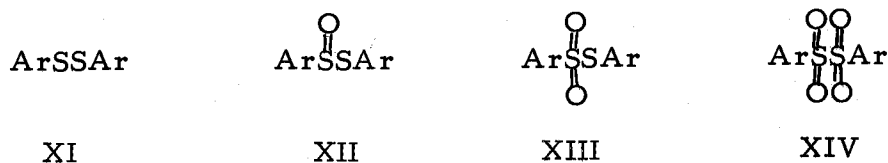
$$d(\text{ArSO}_2\text{H})/dt = k_{\text{obs.}} (\text{ArSO}_2\text{H})^2 = 3k_1 (\text{ArSO}_2\text{SOAr}) \quad (\text{Eq. 17a})$$

$$k_{\text{obs.}} = \frac{3k_1 K}{(\text{H}_2\text{O})} \quad (\text{Eq. 17b})$$

overshadowed by the decrease in K . Thus, electron-withdrawing p -substituents in benzenesulfinic acids affect their stabilities in a manner opposite to the stabilities of the corresponding sulfinyl sulfones.

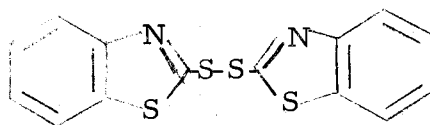
Homolytic Scission of Sulfur-Sulfur Bonds

Probably the most striking feature of the decomposition of sulfinyl sulfones is the fact that they undergo such a facile homolytic dissociation of the sulfur-sulfur bond. Aromatic disulfides, XI, undergo homolytic dissociation only slowly even at elevated temperatures (69, p. 42-45). The rate of dissociation of one of the more easily dissociated disulfides, 2, 2'-dibenzothiazolyl disulfide, XV,



is $7 \times 10^{-7} \text{ sec.}^{-1}$ at 56° , a rate about one thousandth as slow as that for II at the same temperature (30). p -Tolyl p -toluene

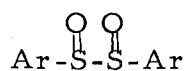
thiolsulfinate, XII ($\text{Ar}-\text{p}-\text{CH}_3\text{C}_6\text{H}_4-$), has been shown to undergo



XV

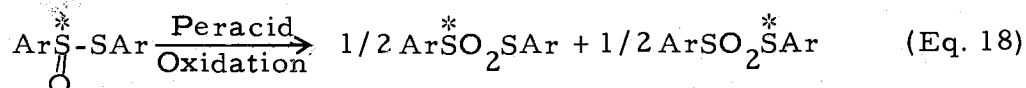
homolytic scission of the sulfur-sulfur bond at 50° at a rate about 4000 times slower than the rate for II (56). There are no reports of a facile homolytic dissociation of the sulfur-sulfur bond in aromatic thiosulfonates, XIII. The chemistry of aromatic α -disulfones, XIV, has not been studied extensively, but there are no reports that indicate that they are thermally unstable. It is reported (12) that p-toluenesulfonyl p-tolyl sulfone melts at 212° , but no mention of any decomposition at this temperature was made.

Aromatic α -disulfoxides, XVI, are totally unknown as a class

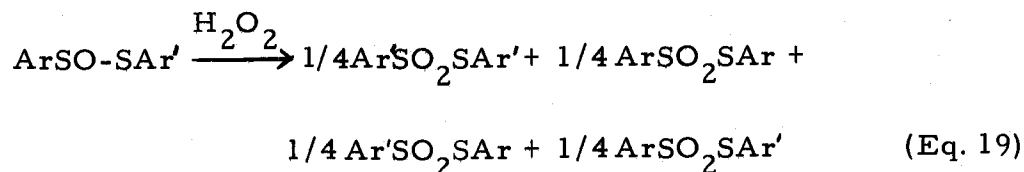


XVI

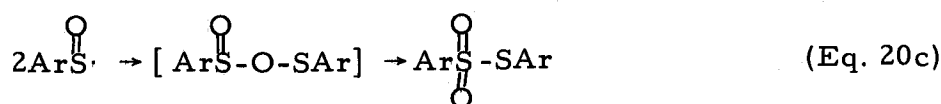
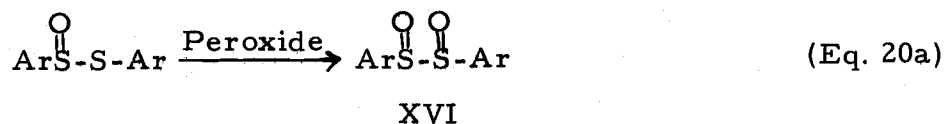
of compounds (38, p. 170; 78). Barnard and Percy (5) have oxidized aromatic thiosulfinates with peracids to aromatic thiosulfonates. They found that when a thiosulfinate in which a sulfur was isotopically labelled was used the resulting thiosulfonate was randomly labelled (Eq. 18). Also, hydrogen peroxide oxidation of asymmetrically substituted thiosulfinates led to a mixture of all possible



asymmetrically and symmetrically substituted thiosulfonates (Eq. 19).



The work of Topping and Kharasch (78) indicates that the coupling of arenesulfinyl radicals leads to the thiosulfonate. In view of the above reports it seems quite plausible that the oxidation of thiosulfinates to thiosulfonates occurs by the mechanism shown in Eq. 20. If Eq. 20 is the correct mechanism, which is strongly indicated, then



the homolytic scission of the sulfur-sulfur bond in α -disulfoxides is even more facile than the same process in sulfinyl sulfones. This would explain why α -disulfoxides have never been isolated and thus are unknown.

Topping and Kharasch (78) have generated sulfinyl radicals, $\text{ArSO} \cdot$, in solution at room temperature from the thermal decomposition of sulfenyl nitrates (Eqs. 21). The analogous

thermal decomposition of ethyl nitrate occurs at 200°. The



sulfinyl radicals so generated (Eq. 21a)• seem totally unreactive towards a variety of solvents. In the present work too, it was noted that the sulfinyl radicals produced from the decomposition of II were unreactive towards solvent and olefin. These observations suggest that possibly sulfinyl radicals are a rather low in energy species.

Thus, among the known compounds containing a single sulfur-sulfur linkage the sulfinyl sulfones appear to be unique in their ability to undergo an extremely facile dissociation of the sulfur-sulfur linkage. In part, this facile decomposition results from the unfavorable repulsion between the two adjacent, electron-deficient sulfur atoms (see Figure I, page 45) which leads to an increase of the free energy of the sulfinyl sulfone. The effects of p-substituents in benzene sulfinyl sulfones conform to this concept--electron-withdrawing chlorine accelerates the rate of decomposition while the electron-donating methyl retards it.

However, repulsion between the two sulfur atoms cannot be the only factor responsible for the facile decomposition of sulfinyl sulfones, for if it were, one would expect a -disulfones to decompose more easily than the sulfinyl sulfones, which they do not. Therefore there must be some other factor contributing to this facile

homolysis. It seems reasonable to assume that the other factor is due to $\text{ArSO}\cdot$ radicals being a species of significantly lower energy than $\text{ArSO}_2\cdot$ or $\text{ArS}\cdot$ radicals. This plus the dipole repulsion could explain why sulfinyl sulfones, and apparently α -disulfoxides, decompose so readily.

EXPERIMENTAL

Materials

p-Toluenesulfinic Acid. Sodium p-toluenesulfinate was prepared as described in "Organic Syntheses" (35, p. 492) and recrystallized four times from water. This sodium salt was dissolved in water and filtered; then the acid was precipitated by adding 6 M sulfuric acid and removed by filtration. The acid was then twice recrystallized by dissolving it in the minimum amount of ether, and slowly adding an equal volume of hexane to precipitate the acid. The sulfinic acid was dried in a vacuum desiccator at a pressure of 0.1 mm., and stored in a desiccator at -20°. The acid's melting point was 85° (literature value (42), m.p. 85°).

Sodium Benzenesulfinate. (Aldrich Chemical Company, Inc.). Sodium benzenesulfinate was dried at 175-180° (0.1 mm.).

Benzenesulfinyl Chloride. Thirty grams of sodium benzenesulfinate and 150 ml. of distilled hexane were stirred with a Teflon-covered magnetic stirring bar while thionyl chloride was slowly added until gas no longer evolved from the solution. Then 1.5 ml. additional thionyl chloride was added. The hexane solution was filtered and the hexane was distilled off under water aspirator vacuum at the lowest possible temperature. After the hexane was removed, the

resulting liquid was put under a vacuum of 0.1 mm. and warmed to 50° for 30 minutes. The product was used immediately.

Benzenesulfinyl Phenyl Sulfone. Twenty-six grams of sodium benzenesulfinate was slowly added in portions to 26 g. of benzenesulfinyl chloride in 30 ml. anhydrous ether. This mixture was triturated for 30 minutes, during which time its temperature was kept at 0°. The mixture was filtered, twice triturated with anhydrous ether and filtered, triturated with ice water and filtered using a rubber dam, triturated with ether and filtered, twice triturated with ice water and filtered, three times triturated with anhydrous ether and filtered. The sulfinyl sulfone, m. p. 78°, was left overnight in a vacuum desiccator at 0.1 mm. Infrared spectra showed the product to be identical with some prepared by the method of Knoevenagel and Pollack (52), m. p. 66-67°. The product was stored in a desiccator at -20° C.

p-Toluenesulfinyl p-Tolyl Sulfone (II). p-Toluenesulfinyl p-tolyl sulfone was prepared and purified as described by Brederick and co-workers (11). The sodium p-toluenesulfinate used was dried at 185° and 0.1 mm. It was found that a purer product was obtained if at slight excess of the sulfinyl chloride over the sodium sulfinate was used in the preparation. This excess was removed by twice triturating the product with anhydrous ether before triturating with water. Infrared spectra showed it to be identical to the spectra published by

Bredereck and co-workers (11). Melting point of the sulfinyl sulfone was 87° , (literature value (11), m.p. 87°). The product was stored in a desiccator at -20° .

2-Naphthalenesulfinyl 2-Naphthyl Sulfone. 2-Naphthalenesulfinyl 2-naphthyl sulfone was prepared and purified as described by Breder-
eck and co-workers (11). It was found that a purer product was ob-
tained if a slight excess of the sulfinyl chloride over the sodium
sulfinate was used in the preparation. This excess was removed by
twice tritulating with anhydrous ether before tritulating with water.
The product melted sharply at 104° , (literature value (11), m. p.
 91°). Infrared spectra showed the product to be pure. It was stored
in a desiccator at -20° .

p-Chlorobenzenesulfinyl p-Chlorophenyl Sulfone. p-Chloro-
benzenesulfinyl p-chlorophenyl sulfone was prepared and purified as
described by Bredereck and co-workers (11). It was found that purer
product was obtained if a slight excess of the sulfinyl chloride over
the sodium sulfinate was used in the preparation. This excess was
removed by twice tritulating the product with anhydrous ether before
tritulating with water. The product melted sharply at 94.5° , (litera-
ture value (11), m. p. 95°). Infrared spectra showed the product to
be pure. It was stored in a desiccator at -20° C.

Methyl Methacrylate. Methyl methacrylate monomer (Aldrich
Chemical Company, Inc.) was purified as described by Kice (40). It

was distilled on a spinning band column under nitrogen, collecting only the middle fraction. This middle fraction was stirred with powdered calcium hydride; it was then distilled from the calcium hydride under nitrogen, b. p. 43° (94 mm.), (literature value (40), b. p. 43° (90 mm.)). The purified methyl methacrylate was stored in a glass-stoppered flask at -20°C .

Azobis-isobutyronitrile. Commercial azobis-isobutyronitrile was recrystallized from distilled methanol, m. p. 103° .

1,1-Diphenylethylene. 1,1-Diphenylethylene was prepared according to the procedure given in "Organic Syntheses" (35, p. 226). It was then stirred for 24 hours over powdered calcium hydride and distilled from calcium hydride at $139-146^{\circ}$ (20 mm.). It was redistilled, b. p. $70-74^{\circ}$ (0.2 mm.), and then stored in a glass-stoppered flask in a desiccator at -20°C .

Galvinoxyl. Galvinoxyl was prepared according to the procedure given by Kharasch and Joshi (39). It was dissolved in hot ethanol, filtered, the filtrate cooled and the product filtered off. The galvinoxyl was dried in a vacuum desiccator at 0.3 mm., m. p. 158° , (literature value (39), m. p. 157.5°).

Hydrogalvinoxyl. Hydrogalvinoxyl was prepared according to the procedure given by Kharasch and Joshi (39). It was chromatographed on acid-washed alumina, eluting with distilled benzene. The benzene was distilled off under reduced pressure and the

hydrogalvinoxyl recrystallized from an ethanol-water mixture. After drying at 0.3 mm. it melted at 156-157°, (literature value (39), m.p. 158-159°).

2,4-Dinitrobenzenesulfonyl Chloride. 2,4-Dinitrobenzenesulfonyl chloride, m.p. 96°, was prepared according to the procedure given by Kharasch and Langford in "Organic Syntheses" (64, p. 47).

p-Toluenesulfonyl Chloride. p-Toluenesulfonyl chloride was prepared according to the procedure given in "Organic Syntheses" (25, p. 99). The product, a red liquid, distilled at 68-75° (1 mm.), (literature value (25, p. 99), b.p. 82-84° (3.5 mm.)).

Silver p-Toluenesulfonate. (Aldrich Chemical Company, Inc.) Silver p-toluenesulfonate was used as received.

Nitrogen. (The Matheson Company) Before use, prepurified grade nitrogen, 99.999% pure, was passed through a tube containing anhydrous calcium chloride, then through a tube containing anhydrous calcium sulfate and indicating anhydrous calcium sulfate, then through a glass-fiber filter, and finally through a trap containing mineral oil.

Solvents

Acetic Acid. Five pounds of reagent grade acetic acid was refluxed with one pound of reagent grade acetic anhydride for 24 hours. The acetic acid was then carefully fractionated from its anhydride on

an Oldershaw column containing 22 theoretical plates, b. p. 117° .

Dioxane. Reagent grade dioxane was purified by the method suggested by Wiberg (79, p. 245) and distilled on an Oldershaw column containing 22 theoretical plates. It was stored over the sodium ketyl of benzophenone which keeps it anhydrous and peroxide free. The dioxane was distilled from the deep blue sodium ketyl as it was needed, b. p. 101° .

Acetonitrile. Reagent grade acetonitrile was refluxed over and distilled from calcium hydride through a 4 ft. glass helices-packed column. It was then refluxed over and distilled from phosphorus pentoxide through a 4 ft. glass helices-packed column, b. p. 82° .

Procedures

Procedure for Kinetic Runs. A weighed amount of the sulfinyl sulfone was dissolved in the appropriate solvent. If sulfinic acid was to be used in the run, a known weight of it was then added, and the solution was diluted to the desired volume. The solution was placed in the previously dried and deaerated kinetic apparatus shown in Figure II and deaerated with dry nitrogen.

The apparatus shown in Figure II is a 100 ml. round-bottom flask fitted with a gas inlet tube, a condenser, and buret. A series of three-way stop-cocks, one between the buret and condenser and one between the buret and flask, allows one to take samples of a

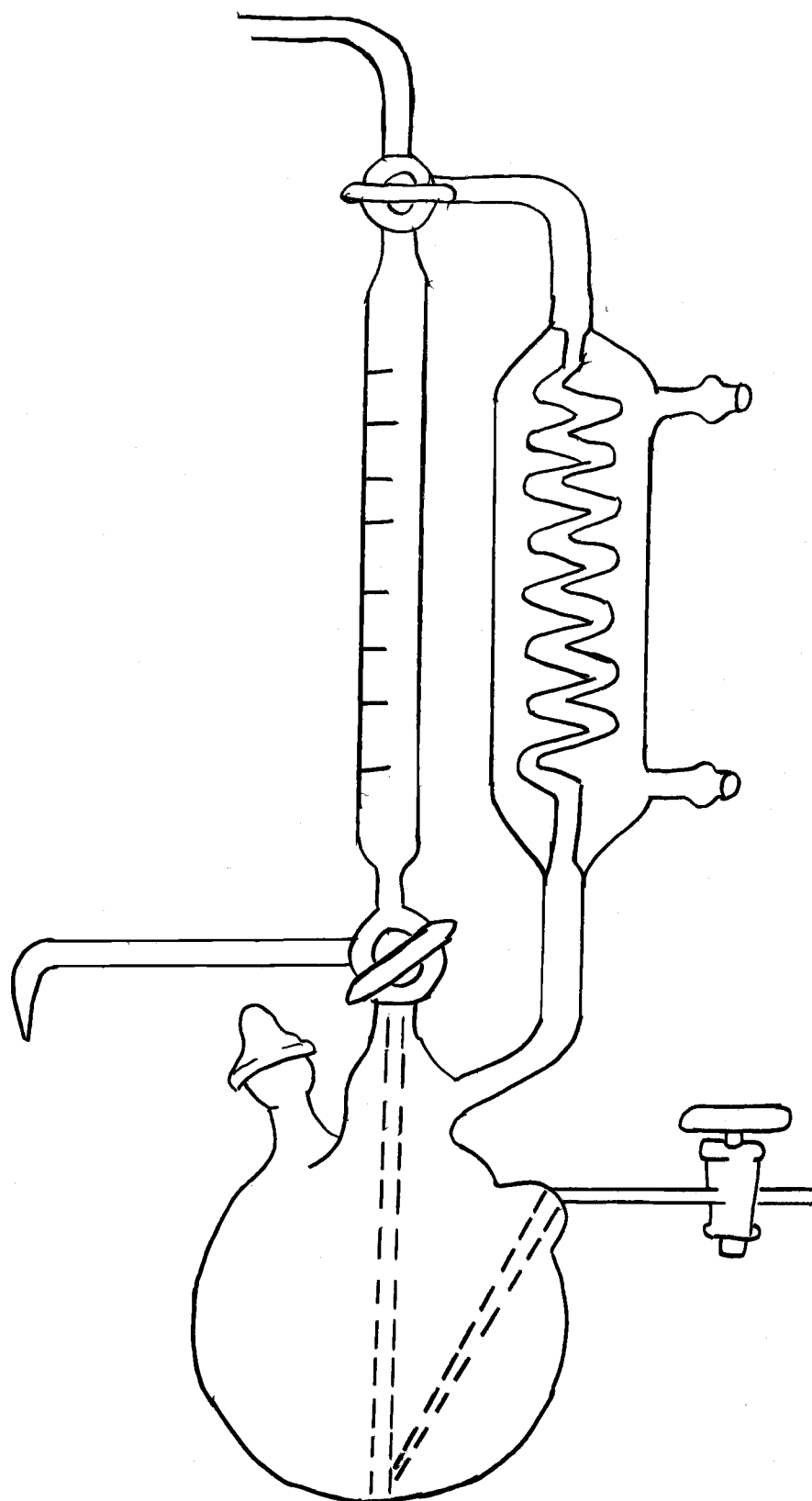


Figure II

known volume without exposing the solution to the atmosphere.

After five to ten minutes deaeration, the kinetic apparatus was placed in a constant temperature bath and a 5 ml. sample was removed and run directly into 2 ml. of 1.5 N aqueous sulfuric acid. To this 13 ml. more of 1.5 N aqueous sulfuric acid was slowly added; adding the sample in this fashion to the aqueous acid hydrolyzes the sulfinyl sulfone to sulfinic acid without precipitating it. The amount of sulfinic acid from the sample was then determined by titration with 0.200 N sodium nitrite. The procedure for titration of sulfinic acid by standard sodium nitrite is as follows: The acid solution of sulfinic acid is stirred with a Teflon-covered magnetic stirring bar while a 10 ml. microburet, with its tip below the surface of the solution, is used to add small portions of standard nitrite solution. After the addition of each portion of nitrite solution (0.01 ml.), a glass rod is used to remove a small drop of the solution and touch it to a strip of potassium iodide-starch paper. The end-point of the titration is reached when a drop of the solution produces a faint pink color on the iodide-starch paper within five seconds. This method has an indicator blank of 0.01 ml. Control experiments demonstrated that the products of the decomposition do not interfere with the titration. Titration of weighed samples of pure sulfinic acid demonstrated that the method is accurate to 0.01 ml.

Samples were taken in the above manner throughout the entire

course of the decomposition. In addition, a last sample was taken after ten half-lives. The volume, V_{∞} , of the nitrite solution required to titrate this last sample after total decomposition was zero unless excess sulfinic acid had been added. The volume of the nitrite solution used to titrate the initial sample is represented by V_0 and the volume of the nitrite solution used on a given sample is represented by V . For each run, the values of $\log (V - V_{\infty} / V_0 - V_{\infty})$ were plotted against time. Good linear plots were obtained and from the slope of these plots, the first-order rate constants were calculated.

In runs with a large excess of added sulfinic acid the infinity titer, V_{∞} , drifted slowly downward due to the disproportionation of the residual sulfinic acid. This rate of disproportionation was slow enough, compared to the rate of the decomposition of the sulfinyl sulfone, that it was easy to estimate what the infinity titer would have been in the absence of any disproportionation and also to correct the measured titration volumes, V , of the samples for the small amount of disproportionation which occurred during the decomposition of the sulfinyl sulfone. This correction was performed in the following manner: The drift in infinity titer was plotted against time. After several points, a curve was established. This curve was extrapolated back to zero. From this curve one could estimate at any time, the amount of disproportionation which had taken place.

Product Studies. The product studies were carried out in a

manner similar to the kinetic runs. However, there was a slight modification. A distillation apparatus was connected to the kinetic apparatus and the entire system swept with dry nitrogen and flamed with a Bunsen burner to remove any moisture in the surface of the glass. After the apparatus had cooled, a weighed amount of the sulfinyl sulfone was placed in the kinetic apparatus, and for those runs in which sulfinic acid was also to be used, a weighed amount of it also. Dioxane was distilled into the apparatus from the sodium ketyl of benzophenone. This rigorously anhydrous solution was then decomposed at 50° in the same manner as the kinetic runs. After total decomposition, a measured sample was titrated with standard nitrite solution to determine the residual sulfinic acid, if any. Two more aliquots were removed, slowly added to water, and titrated to the bromothymol blue end point with 0.100 N sodium hydroxide. Another aliquot was added to anhydrous ether, the ether extracted twice with water and the combined water layers titrated with 0.100 N sodium hydroxide to the bromothymol blue end point. Control experiments prove that by this latter procedure p-toluenesulfonic acid anhydride remains completely in the ether layer while any p-toluenesulfonic acid is completely transferred to the water layer.

The volume of the remainder of the decomposition solution was measured, and the solution was then slowly diluted ten times its volume of water. This resulting mixture was extracted three

times with ether. The ether extracts were combined and washed with dilute sodium bicarbonate and then with water. This ether solution was dried over anhydrous sodium sulfate and the ether evaporated off under reduced pressure. The residue was chromatographed on acid-washed alumina using as eluents successively, hexane, hexane-benzene mixtures, benzene, benzene-ether mixtures, and finally pure ether. The eluting solvents were collected in many fractions, and the solvents were evaporated off under reduced pressures. First to be eluted off the alumina column when any was present was p-tolyl disulfide, which washed off immediately with hexane. Next, p-tolyl p-toluenethiolsulfonate was eluted off the column in 25 percent hexane - 75 percent benzene. Traces of unidentifiable oils came off throughout the chromatography.

The aqueous layer from the decomposition solution was evaporated to dryness under vacuum. The residue was a violet colored solid, p-toluenesulfonic acid.

Product Studies from the Decomposition of II in the Presence of Diphenylethylene. Decomposition of II in the presence of 1, 1-diphenylethylene was carried out similarly to the kinetic runs except that at the start 15.6 g. of the olefin was added and the total solution was diluted to 50 ml. At the end of the decomposition, titration of a sample showed no sulfinic acid to be present.

The remaining solution was dumped into ten times its volume

of water and the mixture was extracted three times with ether. The ether extracts were washed with dilute sodium bicarbonate and dried over sodium sulfate. The ether was evaporated off under reduced pressure and the residue was chromatographed on a 3 cm. \times 26 cm. column of acid-washed alumina using as eluents successively hexane, hexane-benzene mixtures, benzene, benzene-ether mixtures, and finally ether. The eluting solvents were collected in small fractions and evaporated off under reduced pressure.

First eluted off the column with hexane was unreacted 1, 1-diphenylethylene. Next off, with 60 percent hexane-40 percent benzene, was 0.19 g. of p-tolyl 2, 2-diphenylvinyl sulfide, IV, m. p. 82-83° (68). Next off, with 20 percent hexane-80 percent benzene, was 0.22 g. of p-tolyl p-toluenethiolsulfonate. Next off, with 80 percent benzene-20 percent ether, was 0.24 g. of p-tolyl 2, 2-diphenylvinyl sulfone, III, m. p. 102-103° (68). All fractions off the column contained small traces of unidentifiable yellow oils. The identity of these compounds is proven on page 69.

The above procedure was repeated using p-tolyl p-toluenethiolsulfonate and p-toluenesulfonic acid in place of II. The reaction solution was worked up in an identical manner as described above. From the chromatogram the only compounds obtained were unaltered 1, 1-diphenylethylene and p-tolyl p-toluenethiolsulfonate.

The above procedure was repeated using p-toluenesulfinic acid

in place of II. The reaction solution was worked up in the same manner as described above. The products from the chromatography were different from those obtained from the decomposition of II in the presence of 1, 1-diphenylethylene. A new product which was eluted by 80 percent benzene-20 percent ether, was p-tolyl 1, 1-diphenylethyl sulfone, V, m. p. 129-130°.

Galvinoxyl Studies. Because preliminary experiments indicated that p-toluenesulfinic acid reacted quite rapidly with galvinoxyl, II was treated by a special procedure to insure that it was free of sulfinic acid. One gram of II was dissolved in 25 ml. of dry benzene, and the solution placed on a 1.5 cm. \times 10 cm. column of 50 percent anhydrous magnesium sulfate-50 percent Celite. Both the magnesium sulfate and the Celite were washed successively with distilled ether and dried at 800° for eight hours before use. The column was eluted with 25 ml. of benzene and then the next 25 to 30 ml. of eluate was collected and evaporated to dryness under vacuum below room temperature. The residue was then kept for one hour at room temperature and 0.1 mm. pressure. A small amount was weighed, hydrolyzed, and titrated with standard sodium nitrite as in the kinetic runs. It was found to be 35 percent decomposed. p-Toluenesulfinyl p-tolyl sulfone, II, purified in this manner gave good initial zero-order kinetics for the disappearance of galvinoxyl. Without this treatment the initial rate of disappearance of

galvinoxyl was sometimes faster and not always zero order in galvinoxyl.

The galvinoxyl studies were carried out in the apparatus shown in Figure III. A weighed sample of II was placed in tube A (Figure III), and 5 ml. of a solution of a known concentration of galvinoxyl in dioxane was pipetted into tube B (Figure III). The apparatus was connected to a vacuum line, swept out with dry nitrogen, the contents frozen at -80° , and stopcock D was then opened. After the apparatus had been evacuated, the stopcock was closed, and the contents were thawed. This degassing was repeated, then dry prepurified nitrogen was admitted to the apparatus. The stopcock was closed and the apparatus removed from the vacuum line. The II in A was dissolved in the solution in B and the solution was allowed to flow into cell C. Cell C is a standard one centimeter Beckman Pyrex cell. The apparatus was immediately placed in the cell compartment of a Beckman Model DB spectrophotometer which was thermostated at 29.3° . The disappearance of galvinoxyl was followed by measuring the change in optical density at 570 m μ .

Attempted Preparation of a Sulfenyl Sulfonate. 2,4-Dinitrobenzenesulfenyl chloride was dissolved in anhydrous acetonitrile in the round bottom flask, F, shown in Figure IV. Nitrogen was bubbled through the solution via the gas inlet tube A. A slurry of silver p-toluenesulfonate was added through the addition funnel, B,

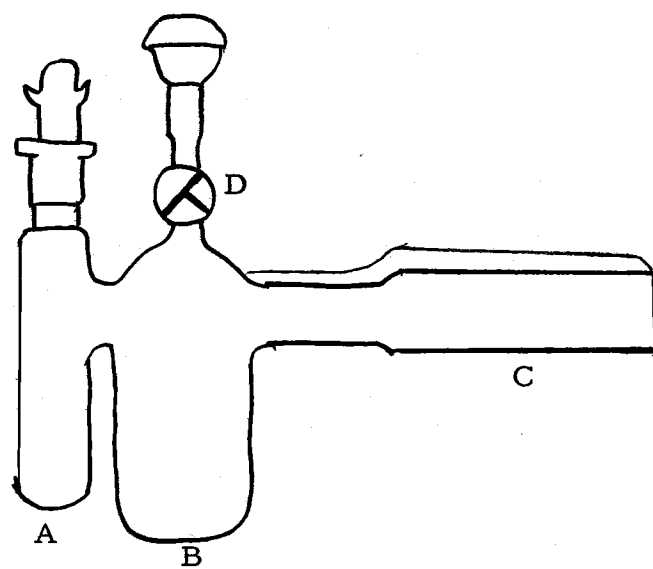


Figure III

while the mixture was stirred by a Teflon-covered magnetic stirring bar. During this addition the apparatus was kept in a dry ice-acetone bath. Dry ice was added slowly enough so that the solvent would not freeze. During the addition the solution turned from a yellow color to a bright yellow-green color. After the addition was completed, the apparatus (Figure IV) was inverted and the silver chloride which had formed during the addition was filtered off on the sintered glass disc D, while the solution ran into flask C which was submerged in an ice bath. Immediately after this filtration, 2,4-dinitrophenyl disulfide began to precipitate from the solution. A sintered glass disc, similar to D but in a reverse direction, was quickly inserted into flask C and the disulfide was filtered from the solution. The solution was then evaporated under reduced pressure and well below room temperature. A thick yellow oil was obtained. Upon contact with a glass rod, chloroform, or Nujol, this thick yellow oil turned to yellow tar which proved impossible to chromatograph.

The above procedure was repeated using ether as the solvent. The results were the same.

The first procedure was repeated in the same manner except that when the silver chloride was filtered off, the solution was run into a large volume of ice water. A thick yellow oil separated, which had properties like those of the first yellow oil.

The first procedure was repeated using p-toluenesulfonyl

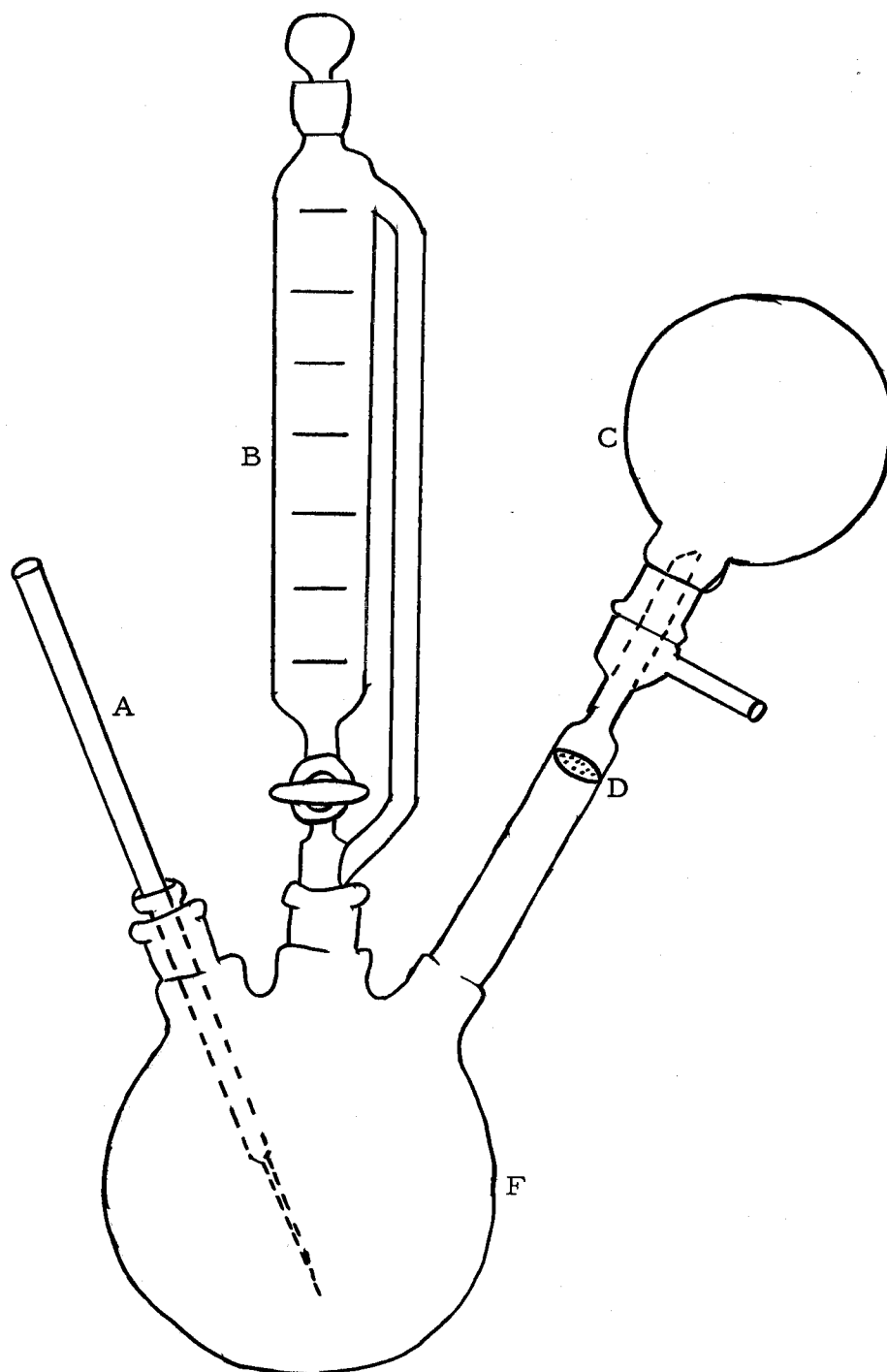


Figure IV

chloride in place of the 2,4-dinitrobenzenesulfonyl chloride. Upon adding silver p-toluenesulfonate to the p-toluenesulfonyl chloride, the solution turned from a yellow color to the deep red color of a fine red wine. Evaporation of the solution after filtering off the silver chloride produced only a yellow tar.

Identification of Products

p-Tolyl p-Toluenethiolsulfonate. The infrared spectra of the samples of p-tolyl p-toluenethiolsulfonate isolated in the present work were identical with the infrared spectra of known samples of the thiol ester and with the spectrum reported in the literature (11). The melting point, 76° , (literature value (42), m. p. 76°), was unsuppressed by mixing it with known samples.

Di-p-Tolyl Disulfide. The infrared spectra of the samples of di-p-tolyl disulfide isolated in the present work were identical with the infrared spectra of known samples of the disulfide and with the spectrum reported in the literature (11). The melting point, 46° , (literature value (43), m. p. $45-46^{\circ}$), was unsuppressed by mixing it with known samples.

p-Toluenesulfonic Acid. The properties of p-toluenesulfonic acid, isolated from the decomposition, were identical in every way with those of a known sample. The dihydrate melted at 104° , the anhydrous acid melted at $40.5-44^{\circ}$. The infrared spectrum of the

p-toluenesulfonic acid and of its p-toluidine salt matched the infrared spectrum of known samples. Melting point of the p-toluidinium p-toluenesulfonate was 196-198°, (literature value (33, p. 140), m. p. 197°.

p-Tolyl 2, 2-Diphenylvinyl Sulfone, III. The infrared spectrum of III isolated from the decomposition of II in the presence of diphenylethylene showed strong adsorption at 1325 cm.^{-1} and 1150 cm.^{-1} . The n. m. r. spectrum showed no resonance between 4-10 τ except for a singlet attributed to the p-tolyl methyl group at 7.67 τ (intensity, 3). The other resonances were a complex pattern attributed to the aromatic protons between 2.4 τ and 3.0 τ (intensity, 14.5) and a sharp singlet attributed to the vinyl proton at 3.1 τ (intensity, 1). The ultraviolet absorption spectrum in 95 percent ethanol showed λ_{max} at 274 $\text{m}\mu$ ($\epsilon=18,200$). For comparison, phenyl 2-phenylvinyl sulfone has λ_{max} at 275 $\text{m}\mu$ ($\epsilon=26,200$)(4). The molecular weight of III in chloroform, as measured on a Mechrolab Vapor Pressure Osmometer Model 301, was 331 (calculated value, 334). The melting point of III was 102-103°, (literature value (68), m. p. 103-103.5°).

Anal. Calculated for $\text{C}_{21}\text{H}_{18}\text{O}_2\text{S}$: C, 75.43; H, 5.43; S, 9.57. Found: C, 74.93; H, 5.73; S, 9.40.

p-Tolyl 2, 2-Diphenylvinyl Sulfide, IV. The n. m. r. spectrum of the sample of IV isolated from the decomposition of II in presence of diphenylethylene showed no resonance between 4-10 τ except for

a singlet attributed to the p-tolyl methyl group at 7.67 τ (intensity, 3). The other resonances were a complex pattern attributed to the aromatic protons between 2.4-3.0 τ (intensity, 14) and a sharp singlet at 3.3 τ (intensity, 1). The ultraviolet spectrum in 95 percent ethanol showed a λ_{max} at 310 m μ ($\epsilon=24,000$). The melting point of IV was 82-83°, (literature value (68), m. p. 84°).

Anal. Calculated for $\text{C}_{21}\text{H}_{18}\text{S}$: C, 83.50; H, 5.95; S, 10.6.
Found: C, 83.46; H, 6.03; S, 10.82.

p-Tolyl 1,1-Diphenylethyl Sulfone, V. The infrared spectrum of the sample of V, m. p. 129-130, isolated from heating p-toluenesulfinic acid in the presence of diphenylethylene showed strong absorption at 1140 cm.^{-1} and a strong doublet around 1305 cm.^{-1} . The n. m. r. spectrum of V showed a sharp singlet at 8.03 τ (intensity, 3) due to the methyl on the tetrasubstituted carbon. At 7.75 τ (intensity, 3) a sharp singlet also appeared, due to the p-tolyl methyl group. Between 2.4 τ and 3.0 τ (intensity, 13.5) a complex pattern was exhibited attributed to the aromatic protons. The ultraviolet spectrum showed λ_{max} at 273 m μ ($\epsilon = 17,000$). The molecular weight, as determined from one dilute sample in chloroform on a Mechrolab Vapor Pressure Osmometer Model 301, was 326 (calculated value, 336).

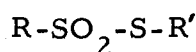
Anal. Calculated for $\text{C}_{21}\text{H}_{20}\text{O}_2\text{S}$: C, 75.09; H, 5.95; S, 9.52.
Found: C, 74.82; H, 5.75; S, 9.73. The melting point was 129-130°C.

Di-2, 4-Dinitrophenyl Disulfide. Di-2, 4-dinitrophenyl disulfide was identical in every respect with a known sample; their infrared spectra were identical. This disulfide melts above 260°C.

II. THE THERMAL DECOMPOSITION OF THIOLSULFONATES

INTRODUCTION

Thiolsulfonates, XVII, have been known for at least 100 years (60). During much of their history, many workers believed these compounds were disulfoxides, XVIII. The structure of a mixed sulfinic-sulfenic anhydride, XIX was also a possibility.



XVII



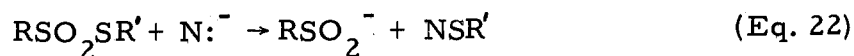
XVIII



XIX

In 1951, Cymerman and Willis (29) published the infrared spectra of a number of aromatic disulfides, disulfones and thiolsulfonates. From these infrared spectra they were able to determine the characteristic absorption frequencies for the S-O, C-S, and S-S linkages. They demonstrated, quite convincingly that thiolsulfonates have the structure of the thiol ester of a sulfonic acid, XVII. It is now apparent that all compounds with the $\text{-SO}_2\text{-}$ group show two strong absorption bonds in the infrared at about 1150 cm.^{-1} and 1340 cm.^{-1} . Thus, many of the compounds in the early literature which are referred to as disulfoxides are in reality thiolsulfonates.

Thiolsulfonates undergo nucleophilic displacement upon the divalent sulfur atom (Eq. 22). These reactions involving ionic



scission of the sulfur-sulfur bond are well known (38, p. 91). In 1922, the thermal scission of the sulfur-sulfur bond in benzyl α -toluenethiolsulfonate, XVII ($R=R'=C_6H_5CH_2-$), was reported (73). It was reported that this decomposition yielded 0.7 mole of sulfur dioxide per mole of thiolsulfonate decomposed.

This thermal decomposition did not receive further attention until 1960, when Kice and co-workers (32, 44, 46, 47) described a detailed study of this type of reaction. These workers found that on being heated in inert solvents at temperatures ranging from 130-200° alkyl or aryl aralkanethiolsulfonates undergo thermal decomposition. In almost every case sulfur dioxide is liberated in nearly quantitative yield. The other principal product from the decomposition of $R_2CHSO_2SCH_2R'$ is the sulfide R_2CHSCH_2R' . However, the decomposition also yields varying amounts of other products, namely, the hydrocarbons R_2CH_2 , $R'CH=CHR'$ and R_2CHCHR_2 , the disulfide $R'CH_2SSCH_2R'$, the thioketone $R_2C=S$, and possibly the thioaldehyde $R'CH=S$.

Kinetic studies of the thiolsulfonate decomposition show that all of the decompositions so far examined exhibit good first-order kinetics and that their rate is dependent upon the polarity of the solvent used, the decomposition being more rapid in polar solvents than in non-polar solvents (46, 47).

The rate of decomposition of a thiolsulfonate RSO_2SR' depends

markedly upon the nature of the R and R' groups (44, 46, 47). For example, changing R from benzyl to benzyhydril accelerates the rate of decomposition by a factor of about 200. This variation of rate with the nature of the aralkyl group, R, is considerably less than the factor of 10^4 to 10^5 normally observed between benzyl and benzyhydril derivatives in solvolysis reactions (76). Therefore, it is likely that the aralkyl fragment has considerably less carbonium ion character in the transition state of the thiol-sulfonate decomposition than is the case in such typical carbonium ion reactions as solvolysis.

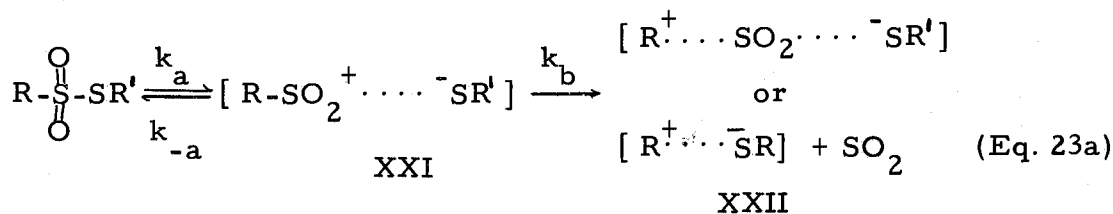
Decomposition of a series of diphenylmethanethiol-sulfonates, $(C_6H_5)_2CHSO_2SR'$, reveals the following dependence of the relative rate of decomposition upon R': R' (relative rate); phenyl (25); benzyl (1.0); methyl (0.3) and n-butyl (0.2). For a series of α -toluene-thiol-sulfonates, $C_6H_5CH_2SO_2SR'$, the dependence of the relative rate upon the nature of R' is as follows: R' (relative rate); benzyl (1); carboethoxymethyl ester, $C_2H_5OOCCH_2^-$ (3.1); phenyl (13). These results show that the dependence of the rate upon the nature of R' parallels the effect of R' on the acidity of R'SH.

Low concentrations (10^{-3} M) of strong acids, such as p-toluenesulfonic acid, bring about very rapid decomposition of diphenylmethanethiol-sulfonates. The principal products of the acid catalyzed decomposition are the same as from the uncatalyzed decomposition.

Decomposing phenyl diphenylmethanethiolsulfonate, XX, in bromobenzene containing styrene does not appear to initiate the polymerization of styrene to any significant extent (47). In fact, the yield of polymer actually decreases slightly as the concentration of the thiolsulfonate is increased. The amount of sulfur dioxide evolved under these conditions showed that the rate of decomposition of XX is practically the same as in the pure solvent.

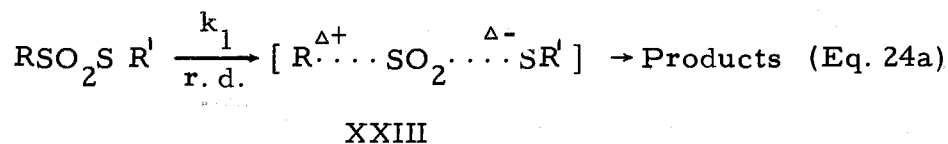
The above observations suggest a mechanism involving heterolytic cleavage of both the C-SO₂ and SO₂-S bonds in the transition state of the rate-determining step. The marked dependence upon the nature of R' for RSO₂SR' suggests that the -SR' function acquires considerable negative charge in this transition state while the rather mild response to the nature of R-, a 170 fold increase on going from benzyl to benzhydryl, suggest that the positive character assumed by R- is of a much lesser magnitude than the full-fledged carbonium ion generated in solvolysis reactions.

One mechanism which was in accord with these facts is shown in Eqs. 23. This involves an initial reversible ionization of the

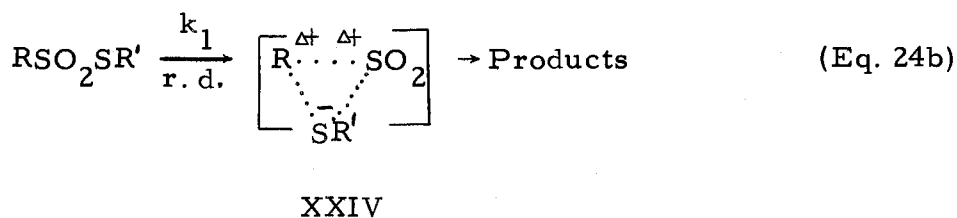


thiolsulfonate to the ion pair XXI, followed by a rate-determining decomposition of XXI to the ion pair XXII. The principal product of this reaction is formed by collapse of XXII.

Another mechanism (46) for the decomposition consistent with the data is a rate-determining ionization of the thiol-sulfonate to an intermediate such as XXIII in Eq. 24. In XXIII, R is not considered to be a full fledged carbonium ion. It is also possible to have rate-determining formation of an intermediate such as XXIV. In XXIV



part of the positive charge is centered on the sulfonyl group.



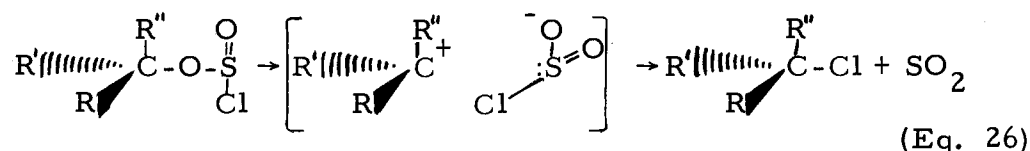
In some respects the thiol-sulfonate decomposition would seem to be related to such internal substitution reaction as the decompositions of chlorosulfites (53), chloroformates (57), and chloroglyoxalates (71) which may be represented as in Eq. 25. Thus all these reactions take an over-all course where Y is some simple stable



molecule such as sulfur dioxide or carbon dioxide. All also tend to proceed more rapidly in better ionizing solvents although the

thiolsulfonate and chloroglyoxalate decompositions are less sensitive in this respect than the other two reactions.

Internal substitution reactions such as the chlorocarbonate and chloroglyoxalate decompositions frequently exhibit considerable stereospecificity. For chlorocarbonates (57) degrees of retention ranging from 15 to 99 percent have been reported. In the chloroglyoxalate decomposition one also observes a high degree of retention (71). The chlorosulfite decomposition has been reported to give both predominant retention (Eq. 26) and predominant inversion (53), depending on the particular compound and the reaction conditions



employed, but in no case has more than 85 percent racemization been reported.

It was therefore of interest to determine the stereochemistry of the decomposition of thiolsulfonates, in order to compare the results with those found for these other S_Ni reactions. Engebrecht (32) achieved this goal by synthesizing optically active phenyl α -toluene-thiolsulfonate- α - \underline{d} , $\text{C}_6\text{H}_5\overset{*}{\text{C}}\text{HDSO}_2\text{SC}_6\text{H}_5$, XXV- α - \underline{d} , and studying the stereochemistry of its decomposition. He found that in any of the solvents studied (bromobenzene, benzonitrile, or methyl benzoate) the decomposition of optically active XXV- α - \underline{d} ($[\alpha]_D^{25} = +0.84$) occurred with a very high degree of racemization. That small part of

of the product (five to 16 percent) which was not racemized was of inverted configuration.

In order to be sure that the observed racemization was not due to the thiolsulfonate undergoing racemization prior to its decomposition Engebrecht partially decomposed a sample of optically active thiolsulfonate XXV- α -d, recovered the undecomposed thiolsulfonate, and determined its rotation. It was found to have undergone no decrease in optical activity. Actually, there appeared to be a slight increase in rotation. One possible explanation for this behavior is that the decomposition of the α -deuterio ester is subject to a small kinetic isotope effect, which causes it to decompose somewhat less rapidly than the undeuterated ester. Partial decomposition of a mixture of the α -deuterio and undeuterated thiolsulfonates, such as the one used by Engebrecht, would then lead to an enrichment of the remaining thiolsulfonate in the optically active α -deuterio compound.

Another possible explanation for the increased rotation of the partially decomposed thiolsulfonate is that the dextrorotatory thiolsulfonate contains a small amount of an impurity, which is either levorotatory or optically inactive, and which decomposes faster than the thiolsulfonate. Partial decomposition and recovery of the undecomposed thiolsulfonate will give a thiolsulfonate fraction which no longer contains this impurity and which will exhibit a correspondingly larger specific rotation.

The purpose of the first part of the present research has been to determine the real source of this small increase in the specific rotation of thiolsulfonate recovered from partial decomposition of mixtures of XXV and XXV- α - \underline{d} and to measure the kinetic isotope effect, if any. Knowledge of the magnitude of any isotope effect would be very valuable in determining the mechanism by which the decomposition takes place.

The principal evidence previously obtained that the thiolsulfonate decomposition is not a radical reaction is the failure of XX to initiate the polymerization of styrene. In the decomposition of XX in the presence of styrene the amount of styrene polymer produced decreased as the concentration of XX was increased, suggesting that there is inhibition associated with XX. It therefore seems prudent to reinvestigate the possibility of radical intermediates using a more dependable method.

RESULTS

Optical Stability of Phenyl α - Toluenethiolsulfonate- α - $\underline{\underline{d}}$

As previously mentioned, when Engebrecht heated a mixture of optically active phenyl α -toluenethiolsulfonate- α - $\underline{\underline{d}}$, XXV- α - $\underline{\underline{d}}$, and the undeuterated ester in solution until 50 percent of the thiol-sulfonate had decomposed and the undecomposed thiolsulfonate was recovered, the recovered material was found to have a slightly higher specific rotation than the starting thiolsulfonate. Two possible explanations can be suggested for this behavior: First, if the decomposition exhibits a kinetic isotope effect the optically active deuterated thiolsulfonate would decompose less rapidly than the non-deuterated thiolsulfonate also present in the sample employed for the experiment. This will cause the thiolsulfonate recovered after 50 percent decomposition to be enriched in the optically active ester. A second possibility is that there is a small amount of a thermally less stable substance present in the starting thiolsulfonate as an impurity. Rapid decomposition of such an impurity could cause the observed effect, particularly if the impurity were optically active and significantly levorotatory.

One can distinguish between these two possibilities by partially decomposing samples of a mixture of optically active XXV- α - $\underline{\underline{d}}$ and

non-deuterated XXV to various extents of reaction and then determining the specific rotation of the recovered undecomposed thiol-sulfonate. If the decomposition exhibits a kinetic isotope effect the ratio of optically active deuterated ester to non-deuterated ester should increase steadily with increasing percent decomposition and the specific rotation of the recovered thiolsulfonate will accordingly increase with increasing percent decomposition.

On the other hand, if the observed effect is due to an impurity which decomposes more rapidly than the thiolsulfonate, the specific rotation of the recovered thiolsulfonate will increase only during the initial stages of the decomposition and will remain constant thereafter.

In the present work samples of Engebrecht's (32, p. 65; run 3) phenyl α -toluenethiolsulfonate- α - \underline{d} , XXV- α - \underline{d} , were mixed with approximately equal portions of the non-deuterated thiolsulfonate, XXV. These samples were decomposed in methyl benzoate at 172° until measurements of sulfur dioxide evolution indicated the desired fraction of thiolsulfonate had decomposed. The undecomposed ester was then recovered and its optical rotation determined. These results are shown in Table VII.

The specific rotation of the thiolsulfonate increases only during the first 40 percent of decomposition. Since no further significant increase in $[\alpha]_D^{25}$ occurs after 40 percent decomposition, one can

Table VII. Optical Stability of Phenyl α -Toluenethiolsulfonate- α - \underline{d} in Methyl Benzoate at 172° .

Weight XXV- α \underline{d} ^{1/}	Weight XXV	Percent decomposed	Sample weight for rotation	$\alpha - \alpha_o$	$[\alpha]_D^{25}$
g.	g.	%	g.	degrees	degrees
0.1046	0.1054	0	0.1846	0.040	0.433 ± 0.02
0.1785	0.1796	20	0.1949	0.043 <u>4</u>	0.451 ± 0.02
0.1994	0.2001	40	0.1904	0.043 <u>5</u>	0.462 ± 0.02
0.3608	0.3604	70	0.1602	0.037	0.462 ± 0.02

^{1/} Consists of 87% α -deuterio ester and 67% undeuterated ester as determined by suitable analyses for deuterium content.

rule out the possibility that the majority of the change is due to an isotope effect which causes the α -deuterio thiolsulfonate to decompose slightly more slowly than the undeuterated and inactive form. Thus it appears that the slight increase in specific rotation is due to a small amount of a thermally unstable impurity in the thiolsulfonate.

Galvinoxyl Studies

The principal evidence that the thiolsulfonate decomposition is not a radical reaction has, up to now, been the failure of several thiolsulfonates to act as initiators of styrene polymerization. Since initiation of the polymerization of an olefin is not the most reliable test for radical intermediates it seemed prudent to reinvestigate the possibility of radical intermediates using a more dependable method. As was pointed out in Part I the stable free radical galvinoxyl has been successfully used on many occasions to scavenge and count short-lived free radicals.

A trial experiment showed that a solution of galvinoxyl in bromobenzene underwent no decrease in optical density on being heated for ten hours at 115°. Phenyl diphenylmethanethiolsulfonate, XX, which decomposes in bromobenzene at this temperature at a reasonable rate, $k_1 = 2.1 \times 10^{-5} \text{ sec.}^{-1}$ (44), was decomposed in the presence of galvinoxyl under a variety of conditions. These

results are shown in Table VIII.

In these experiments it was observed that the rate of fading of the galvinoxyl was strongly influenced by the rate of nitrogen flow through the solution. Specifically, it can be seen in Table VIII that the rate of fading of galvinoxyl was much faster when the nitrogen flow rate to remove the sulfur dioxide was slow than when a rapid flow rate was employed. It can also be seen that increasing the concentration of XX by a factor of five only doubles the rate of fading of galvinoxyl under conditions of rapid nitrogen flow. These observations suggest that rate of removal of the sulfur dioxide from the decomposition of XX has a profound influence upon the rate of fading of the galvinoxyl, thus indicating that, in part, the fading of galvinoxyl is due to some reaction with sulfur dioxide before it is removed from solution.

The value of $k_o / 2k_1(RSO_2SR')_o$, which should remain constant if the only thing causing galvinoxyl to be consumed was reaction with radicals produced from the decomposition, decreases as the concentration of XX is increased even under conditions of rapid nitrogen flow. This means that even under these conditions part of the consumption of galvinoxyl, at least, is due to some reaction with sulfur dioxide. Therefore, the smallest value of $k_o / 2k_1(RSO_2SR')_o$ in Table VIII presumably indicates the maximum possible fraction of the decomposition of XX which yields free radical intermediates.

Table VIII. Decomposition of Phenyl Diphenylmethanethiolsulfonate in Presence of Galvinoxyl in Bromobenzene at 115°.

$(\text{Galvinoxyl})_0 \times 10^3$	$(\text{RSO}_2\text{SR}')_0 \times 10^3$	Rate of N_2 flow	$k_0 \times 10^7$ $\text{M}^{-1}\text{sec}^{-1}$	$k_0/2k_1(\text{RSO}_2\text{SR}')_0$
M	M			
1.1	10.2	rapid	0.35	0.08
1.1	5.1	rapid	0.27	0.13
1.1	5.3	slow	0.88	0.39
1.1	2.7	rapid	0.19	0.17

$(\text{galvinoxyl})_0$ = Initial galvinoxyl concentration

$(\text{RSO}_2\text{SR}')_0$ = Initial concentration of XX

k_1 = First-order rate constant for decomposition of XX, $2.1 \times 10^{-5} \text{sec}^{-1}$

k_0 = Zero-order rate of disappearance of galvinoxyl

This value of 0.08 is so low that it seems likely that even here most of the fading galvinoxyl is due to reaction with sulfur dioxide and that the decomposition of XX does not occur by a radical mechanism to any appreciable extent.

DISCUSSION

When a mixture of optically active phenyl α -toluenethiolsulfonate- α - \underline{d} , XXV- α - \underline{d} , and undeuterated XXV is subjected to partial decomposition the rotation of the recovered thiolsulfonate is found to be slightly higher than that of the starting mixture. The results of the present work, however, indicate that this is not due to a kinetic isotope effect, as was previously thought, (32, p. 40) but rather to a thermally unstable impurity present in XXV- α - \underline{d} . Since XXV- α - \underline{d} was recrystallized several times and spectroscopic analysis indicated that it was quite pure, the thermally unstable impurity is presumably present in very low amount. Accordingly, in order to cause the observed effect it presumably is quite strongly levorotatory.

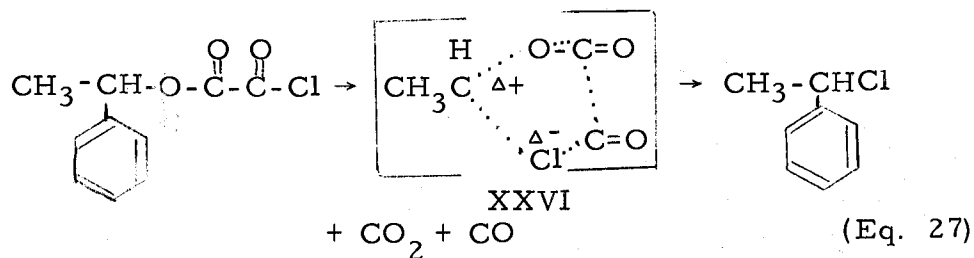
Since the observed effect is not due to a kinetic isotope effect, a mechanism for the thiolsulfonate decomposition involving the scission of the α -CH bond in the rate-determining step, as suggested by Engbrecht (32, p. 40) is no longer acceptable. Any mechanisms of this type would undoubtedly exhibit a sizable primary isotope effect. This being the case, what type of mechanism can one propose for the decomposition of thiolsulfonates?

The dependence of the rate of decomposition on thiolsulfonate structure and solvent ionizing-power suggests that the transition state of the rate determining step possesses some ionic character

with partial negative charge on the sulfide sulfur and partial positive charge on the C-SO₂ bond (44, 46, 47). The galvinoxyl experiments and the failure of thiolsulfonates to initiate the polymerization of styrene both suggest that radicals are not involved to any appreciable extent. The present work indicates that the α -CH bond is not broken in the rate-determining step. These results had previously led Kice and co-workers (46, 47) to note that the thiolsulfonate decomposition has features in common with such S_Ni reactions as the decomposition of chlorocarbonates and chlorosulfites.

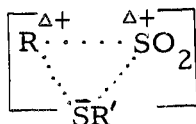
These internal substitution reactions generally exhibit considerable stereospecificity. For examples, chlorocarbonates have been reported to decompose with degrees of retention ranging from 15 to 99 percent (57). The chlorosulfite decomposition has been reported to give both predominant retention and predominant inversion (53) depending upon the particular compound and the reaction conditions employed, but in no case has more than 85 percent racemization been reported.

The thermal decomposition of α -phenylethyl chloroglyoxalate (Eq. 27) also shows considerable stereospecificity giving high degrees



of retention of configuration (71). Like the thiolsulfonate decomposition, the α -phenylethyl chloroglyoxalate decomposition shows less response to changes in solvent ionizing-power than is exhibited by the chlorocarbonate or chlorosulfite decompositions. Because of this Rhoads and Michel proposed a cyclic transition state or intermediate, XXVI, which is less ionic than a true ion pair and more polar than is usually observed for cyclic covalent rearrangements (72).

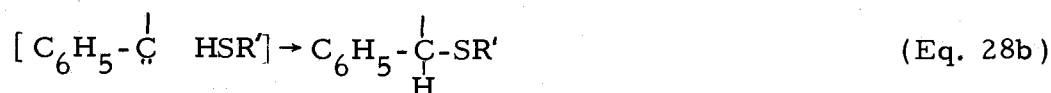
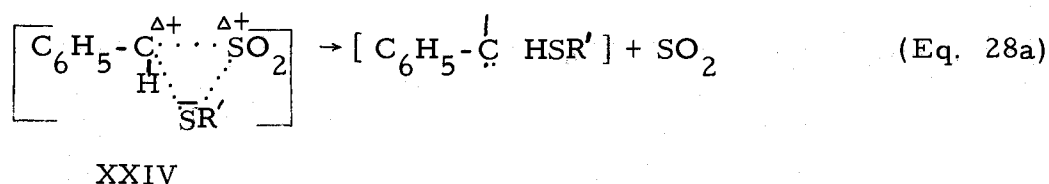
Although there is marked similarity between the thiolsulfonate decomposition and those internal substitution reactions discussed above, the low stereospecificity observed by Engebrecht (32) for the thiolsulfonate decomposition strongly suggests that its mechanism must differ considerably. Even the chloroglyoxalate decomposition, which shows the same dependence on solvent ionizing-power as the thiolsulfonate decomposition, shows a high degree of stereospecificity. It seems, then, highly unlikely that the products from the thiolsulfonate decomposition could arise directly by collapse of an intermediate such as XXIV from Eq. 24b. Having ruled out a mechanism involving



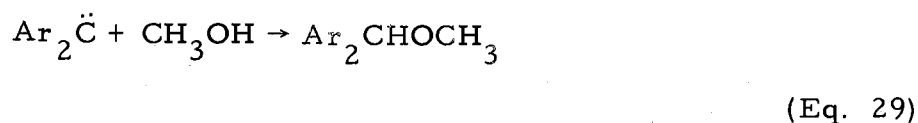
XXIV

radicals, a satisfactory mechanism consistent with the stereochemistry and with the variation of rate with solvent and thiolsulfonate structure is difficult to find.

A possible mechanism consistent with the above results would be the collapse of XXIV to a carbene and mercaptan (Eq. 28). Since all of the thiolsulfonates whose decomposition have so far been investigated have had as R- an aralkyl group with at least one

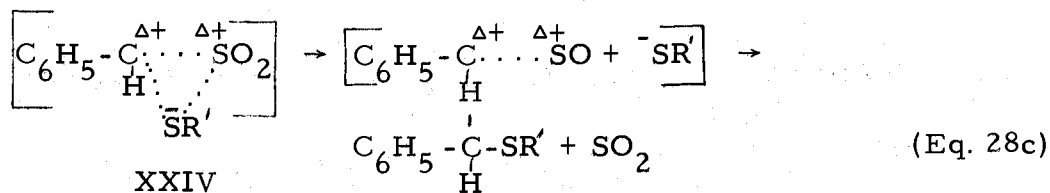


α -hydrogen, it seems conceivable that the mercaptide ion being formed in XXIV could extract a α -hydrogen thus forming a carbene and mercaptan (Eq. 28a). It seems reasonable that a carbene and mercaptan would react together (Eq. 28b) to form a sulfide, since it has been demonstrated (49) that carbenes will react with alcohols to give ethers (Eq. 29).



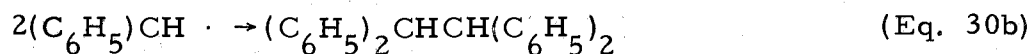
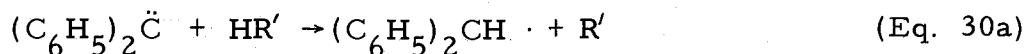
Eq. 28a is not the only route by which XXIV might collapse to give sulfide, the principal product. Thus, XXIV might dissociate to a mercaptide ion and a sulfur dioxide-solvated carbonium ion (Eq. 28c). Since sulfur dioxide should somewhat hinder the approach of the mercaptide ion, it is likely that Eq. 28c should occur with

predominant inversion of configuration. Engebrecht observed (32, p. 29) that decomposition of XXV-a -d did occur with some inversion.



Specifically, XXV-a -d decomposes with 5, 8 and 16 percent net inversion in methyl benzoate, bromobenzene and benzonitrile respectively. Eq. 28c would be expected to compete more effectively with 28a in a better ionizing solvent such as benzonitrile explaining why more net inversion occurs in this solvent.

The reaction illustrated in Eq. 28a has the advantage of being able to explain quite nicely the formation of some of the minor products from certain thiolsulfonate decompositions. For example, in the decomposition of a diphenylmethanethiolsulfonate, $(\text{C}_6\text{H}_5)_2\text{CHSO}_2\text{SCH}_3$, the diphenylcarbene $(\text{C}_6\text{H}_5)_2\ddot{\text{C}}$ could also react as in Eq. 30 with a hydrogen donor to give tetraphenylethane,



which was observed as a minor product in the decomposition of these particular thiolsulfonates. Eq. 30 represents a reaction sequence

which is quite often observed with diphenylcarbene (50). Then again, reaction of a carbene $R\ddot{C}H$ with the mercaptan $HSCH_2R''$ might yield not only the sulfide RCH_2SCH_2R'' , as outlined earlier, but also the hydrocarbon RCH_3 and the thioaldehyde $S=CHR''$. Once formed the thioaldehyde would then either trimerize (70, p. 148) or decompose thermally to olefin $R''CH=CHR''$ and sulfur (70, p. 165).

It must be emphasized that the mechanism proposed in Eq. 28 is only one possibility. The data at present do not allow one to conclude whether or not a carbene is involved in the thiolsulfonate decomposition. However in the absence of better alternatives the mechanism in Eq. 28 is consistent with all of the presently available data.

EXPERIMENTAL

Materials

α - Toluenesulfinic Acid. The method of Engebrecht (32, p. 47) was modified slightly to prepare α -toluenesulfinic acid. Eighty grams of anhydrous sodium sulfite dissolved in the minimum amount of water, 60 g. α -toluenesulfonyl chloride and 400 ml. ether were stirred together in a round bottom flask submerged in an ice bath. The mixture was kept slightly basic at all times by adding small portions of 25 percent sodium hydroxide. After all of the α -toluenesulfonyl chloride had dissolved, the mixture was stirred for one hour. During this hour no more sodium hydroxide was needed to keep the mixture basic. The basic solution was extracted twice with ether. The solution was then cooled and acidified with 6 N hydrochloric acid. A crystalline material first separated. This crystallizing material was filtered, washed with ether and recrystallized twice from a small amount of water. After drying in a vacuum desiccator it melted sharply at 74° , ((literature value (32, p. 47) m. p. $64-68^{\circ}$)). Additional α -toluenesulfinic acid was isolated by extracting the acid solution with ether and evaporating off the ether, but this product was of lower purity than that obtained from the precipitation. Total yield was 28.8 g., 64 percent.

Phenyl α -Toluenethiolsulfonate.(XXV). Benzene sulfenyl

chloride was prepared according to the procedure given in Organic Syntheses (25, p. 99). Seven grams of this sulfenyl chloride was mixed with seven grams of α -toluenesulfinic acid in 100 ml. benzene. After 30 minutes the benzene solution was washed with water, then washed with a saturated solution of sodium bicarbonate, then washed twice more with water. After drying the benzene solution over sodium sulfate, the solvent was removed under reduced pressure. The resulting residue, 43 g., (91 percent) was recrystallized twice from absolute ethanol, then three times from a benzene-hexane mixture and dried in a vacuum desiccator, m. p. 110-112° (literature value 29, 32), m. p. 110-111°).

Phenyl α -Toluenethiolsulfonate- α -d. (XXV- α -d). Phenyl

α -toluenethiolsulfonate- α -d was obtained from R. H. Engebrecht which was a portion of that used in his earlier study of the stereochemistry of the thiolsulfonate decomposition (32). Engebrecht reported for this particular batch of thiolsulfonate; $[\alpha]_D^{25} + 0.837 \pm 0.020$; deuterium content, 0.67 ± 0.04 atoms D per molecule (32, p. 65; run No. 3). The specific rotation, $[\alpha]_D^{25}$, was redetermined and a value of 0.870 ± 0.02 was obtained. The melting point, 110-110.5°, coincided with that reported by Engebrecht (32, p. 65; run No. 3).

Phenyl Diphenylmethanethiolsulfonate. (XX). Phenyl diphenylmethanethiolsulfonate was obtained from J. L. Kice, Oregon State

University, Corvallis, Oregon. This thiolsulfonate was recrystallized three times from ethanol and dried in a vacuum desiccator, m. p. 119-119.5° (literature value (46), m. p. 120-121°).

Galvinoxyl. Galvinoxyl was prepared as previously described (Part I, page 54).

Nitrogen. Nitrogen used was the same as described in part I, page 55.

Solvents

Bromobenzene. (Matheson, Coleman, and Bell). Reagent grade bromobenzene was refluxed over and then distilled from calcium hydride through a four-foot glass helices -packed column. A large middle fraction was collected, b. p. 153.5°.

Methyl Benzoate (Matheson, Coleman and Bell). Reagent grade methyl benzoate was fractionally distilled using a spinning band column, b. p. 85° (14 mm).

Procedures

Optical Stability of Phenyl α -Toluenethiolsulfonate- α - \underline{d} in Methyl Benzoate at 172. A sample of optically active thiolsulfonate $[\alpha]_D^{25} + 0.44 \pm 0.02$ ($\underline{1}$ 1, \underline{c} 9, dioxane) was prepared by diluting optically active thiolsulfonate with $[\alpha]_D^{25} + 0.87$ with an approximately equal weight of undeuterated thiolsulfonate. Portions of this material

were then partially decomposed in methyl benzoate at 172° in the same manner used for earlier kinetic studies of thiolsulfonate decompositions (44; 46; 47; 32, p. 48) until measurements of sulfur dioxide evolution indicated the desired fraction of thiolsulfonate had decomposed. The rate of evolution of sulfur dioxide agreed well with that expected from the known (44) first-order rate constant for decomposition of undeuterated XXV. The reaction was then stopped, and the undecomposed thiolsulfonate was recovered by first removing the solvent at 0.2 mm. pressure and a bath temperature of 40° . The residue was washed three times by boiling it in hexane, then cooling and filtering. The hexane insoluble thiolsulfonate was then recrystallized from benzene-hexane and dried in a vacuum desiccator, m. p. $108-109^{\circ}$. The specific rotation was determined in dioxane using a Rudolph Photoelectric precision polarimeter (0.001°). Recorded readings are the mean of at least 20 readings for the polarimeter tube containing the optically active thiolsulfonate, $\alpha_{\text{rot.}}$, minus the mean of at least 20 readings for the polarimeter tube containing pure solvent, α_0 . All rotations were taken using a one decimeter, center-filled tube having a bore of 4 mm. The results are shown in Table I.

Galvinoxyl Studies. A weighed amount of galvinoxyl was placed into the kinetic apparatus described in Part I, page 56, and shown in Figure II, page 57. A weighed sample of phenyl diphenylethane-thiolsulfonate was dissolved in bromobenzene in a volumetric flask

and the solution was also added to the kinetic apparatus. The solution was deaerated for 20 minutes by a rapid stream of nitrogen and then placed into a constant temperature bath at 115° . During the course of a run the solution was always kept under nitrogen, and aliquots were removed without exposing the remaining solution to the atmosphere.

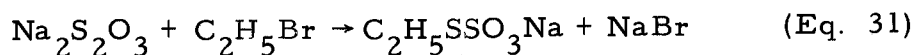
Aliquots were taken directly into a standard one centimeter Beckman Pyrex cell. It was then placed immediately in the cell compartment of a Beckman Model DB spectrophotometer and the optical density of the bromobenzene solution measured at 570 m μ .

Preliminary experiments, carried out in the same manner as above but without the thiolsulfonate, demonstrate that galvinoxyl in bromobenzene at 115° for ten hours undergoes no apparent decrease in optical density.

III. THE ACID HYDROLYSIS OF BUNTE SALTS

INTRODUCTION

In 1874, Bunte (15) prepared sodium S-ethyl thiosulfate (XXVII) by heating an aqueous solution of sodium thiosulfate with ethyl bromide (Eq. 31). Since then the reaction of thiosulfate with organic



halides or the esters of alcohols has been a widely investigated reaction (76). The resulting S-alkyl thiolsulfates are now commonly called Bunte salts.

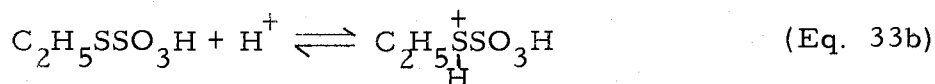
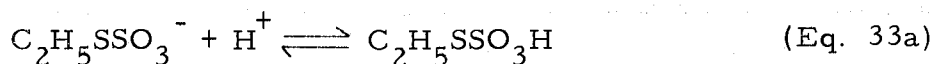
Bunte (15) noted that his sodium S-ethyl thiosulfate, XXVII was susceptible to an acid-catalyzed hydrolysis (Eq. 32). Kice (41) has made a kinetic study of this reaction. The rate of hydrolysis is



clearly first-order in Bunte salt. The rate is much more strongly dependent on acid concentration than any simple proportionality between the rate constant and acid concentration would predict. For example, in water at 63° doubling the hydrochloric acid concentration from 2.88 N to 5.66 N leads to greater than a tenfold increase in rate. Plots of the logarithm of the rate constant against the negative value of the Hammett acidity function, H_0 , are linear and show slopes ranging from 0.99 to 1.04.

To interpret the mechanistic significance of this variation of rate with acid concentration one must have some knowledge of the pK_a of the conjugate acid of the Bunte salt. There are three possibilities: 1) K_a for $C_2H_5SSO_3H$ is very small, 2) K_a for $C_2H_5SSO_3H$ is near unity, or 3) $C_2H_5SSO_3H$ is a very strong acid. The first alternative seems both unlikely and unrealistic since the K_a for sulfamic acid (48), $H_3N^+-SO_3^-$, which should certainly be a weaker acid than $C_2H_5SSO_3H$, is known to be 0.1.

Should K_a for $C_2H_5SSO_3H$ be near unity, the only way to explain the pronounced effect of increasing acid, which persists even at high acidities, would be by assuming that the Bunte salt hydrolysis involves two equilibria (Eq. 33). The second equilibrium would involve



further protonation of the conjugate acid of the Bunte salt

($C_2H_5SSO_3H$) to a species such as $C_2H_5\overset{+}{S}SO_3H$. This would then be the reactive form undergoing hydrolysis. At high acidities at

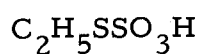
equilibrium essentially all of the Bunte salt would exist as its conjugate acid, and H_0 could be expected to correlate the variation of

$(C_2H_5\overset{+}{S}SO_3H)/(C_2H_5SSO_3H)$ with acid concentration. However, at lower acidities the rate should decrease more rapidly with decreasing

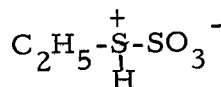
acidity than would be predicted by extrapolation of the rates at higher acidity because at these lower acidities the Bunte salt would no longer be totally in the form of its conjugate acid. Thus at these lower acidities changes in acidity would influence not only the equilibrium in Eq. 33b but also the equilibrium in Eq. 33a. At higher acidities, of course, only the equilibrium in Eq. 33b is noticeably affected by a change in acidity. Kice (41) measured the hydrolysis rate of $\text{C}_2\text{H}_5\text{SSO}_3\text{Na}$ over a wide range of acidities. Comparison of the observed rate constants at low acid concentrations with that calculated by extrapolation from the data at much higher H_0 values shows that the rate at low hydrogen ion concentration is that predicted by extrapolation from the rates at high acidities. Therefore, the dependence of rate on acidity does not change in the manner that would be expected if the conjugate acid of the Bunte salt had a K_a near unity. Kice (41) therefore concluded: "1) $\text{C}_2\text{H}_5\text{SSO}_3\text{H}$ is a very strong acid; 2) the Bunte salt exists at equilibrium in all the solutions almost exclusively as $\text{C}_2\text{H}_5\text{SSO}_3^-$, and 3) increasing concentration of hydrochloric or perchloric acid increases the hydrolysis rate by increasing the small equilibrium concentration of the conjugate acid $\text{C}_2\text{H}_5\text{SSO}_3\text{H}$."

There are two ways in which a Bunte salt could be converted by protonation to a species more reactive towards hydrolysis. One is by protonation on oxygen to give intermediate XXVIII; the other is

by protonation on sulfur to give XXIX. For protonation on oxygen, XXVIII, an A-1 mechanism for the hydrolysis would be unrealistic

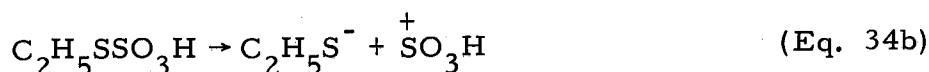
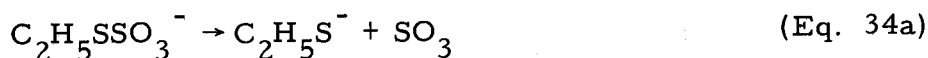


XXVIII

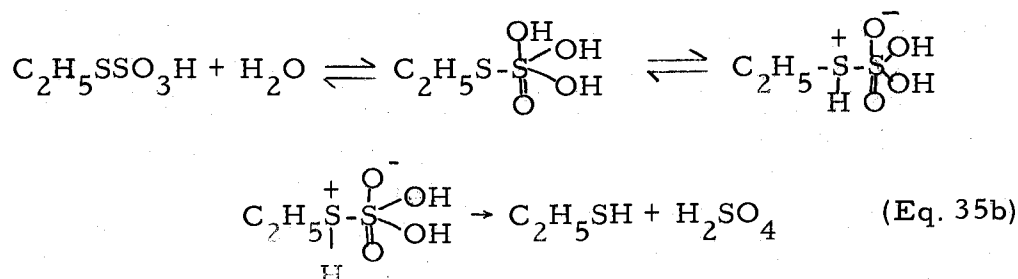
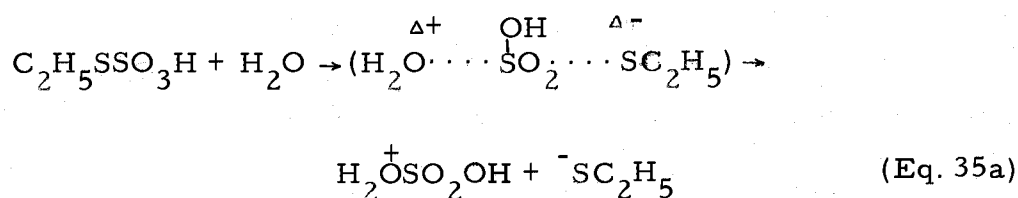


XXIX

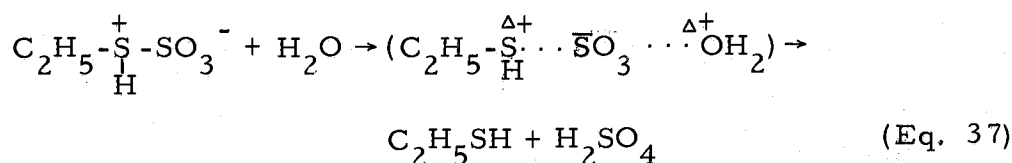
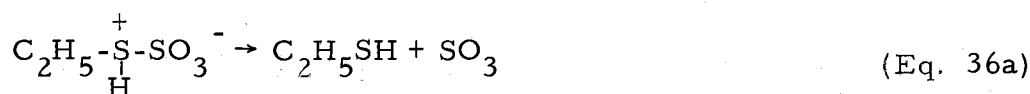
since the Bunte salt itself would be expected to decompose (Eq. 34a) by such a process more readily than would XXVIII (Eq. 34b).



On the other hand since protonation on oxygen reduces the electron density on the sulfate sulfur in XXVIII it renders that atom more susceptible to nucleophilic attack than it was in the Bunte salt itself. If hydrolysis were to involve nucleophilic attack by water on the sulfate sulfur this could explain why the hydrolysis is acid-catalyzed. Such an A-2 mechanism for the hydrolysis could involve either a direct displacement of RS^- from RSSO_3H by water (Eq. 35a), referred to hereafter as an A-2b mechanism, or initial addition of water to XXVIII to give an adduct which then decomposes (Eq. 35b); this latter alternative, which is analogous to the usual mechanism for acid-catalyzed hydrolysis of carboxylic esters, will be referred to as the A-2b' mechanism.



Protonation on sulfur converts the group RS⁻ in the Bunte salt to the much better leaving group $\overset{+}{\underset{\text{H}}{\text{R}}}\text{S}-$ in XXIX. XXIX could then conceivably yield the hydrolysis products via either an A-1 mechanism (Eq. 36) or by an A-2 mechanism (Eq. 37), hereafter referred to as an A-2a mechanism.



Kice (41) demonstrated that while the rate of hydrolysis shows an excellent correlation with H_0 , this does not necessarily mean that the hydrolysis occurs by the A-1 mechanism of Eq. 36. He showed that such a dependence of rate upon acidity could in the present case

be equally consistent with A-2 mechanisms of the type shown in Eqs. 35. This is due to the fact that, strictly speaking, the H_0 acidity function applies only to the equilibria between uncharged bases and their charged conjugate acids. Boyd (9) has demonstrated that the equilibria between negatively charged bases and their acids do not follow the H_0 acidity function exactly. Because of this, it is possible for the effect of a change in strong acid concentration on the equilibrium in Eq. 33 and the effect of the same change on the rate of Eq. 35 to combine to produce an over-all dependence of hydrolysis rate upon acidity which closely parallels the change in the H_0 acidity function.

The purpose of the present work was to obtain information concerning the Bunte salt hydrolysis which might enable one to determine more exactly just which of the mechanisms above is the correct one for the hydrolysis. Useful information for doing this would be the effect of solvent polarity upon the rate and activation parameters for hydrolysis and the effect of changing from water to deuterium oxide upon the hydrolysis rate, particularly if the results of such experiments were then combined with the results of investigations of the effect of changes in Bunte salt structure on hydrolysis rate also being carried out in these laboratories.²

²Anderson, J. Unpublished research. Oregon State University, Corvallis, Oregon. 1965.

RESULTS

Mixtures of dioxane-water are nicely suited for determining the effect of changing solvent upon the rate of acid hydrolysis of a Bunte salt. Dioxane, an inert ether of low dielectric constant, is completely miscible with water, a high dielectric constant solvent. Changing the ratio of water to dioxane not only alters the dielectric constant of the medium but changes the concentration of water, one of the reactants, in the hydrolysis reaction. This dual effect can sometimes lead to ambiguous results for ester hydrolyses.

In the present work the rate of hydrolysis of sodium S-benzyl thiosulfate, XXX, was measured in 40, 60 and 80 percent dioxane-water mixtures at 0.5 M perchloric acid at several different temperatures. The results are shown in Table IX.

The results shown in Table IX show that the rate of hydrolysis of XXX is markedly dependent upon solvent, the rate increasing as the percentage of dioxane is increased. Interestingly, the enthalpy of activation, ΔH^\ddagger , changes only very slightly with solvent. Thus, the effect of solvent upon the rate of hydrolysis is due almost entirely to an entropy effect. Since the enthalpy of activation changes very little and yet the rate increases markedly upon going steadily from 40 to 80 percent dioxane it is obvious, that the entropy of activation must rapidly grow more positive as the percent dioxane is

Table IX. Kinetics of the Hydrolysis of Sodium S-Benzyl Thiosulfate in Dioxane-Water Mixtures.

Temperature (HClO ₄) ° C	M	Dioxane percent	$k \times 10^4$ sec. ⁻¹	
40.1	0.498	80	0.369	
40.1			0.40	
50.0			1.67	
50.1			1.72	
60.0			7.04	$\Delta H^\ddagger = 29.7$ kcal./mole
60.0			7.36	
50.0	0.495	60	0.0638	
60.0			0.368	$\Delta H^\ddagger = 29.7$ kcal/mole
60.0			0.343	
69.8			1.457	
69.8			1.445	
80.0			4.98	
80.0			4.97	
70.0	0.491	40	0.243	$\Delta H^\ddagger = 29.3$ kcal/mole
85.0			1.58	
89.9			2.95	
90.0			2.82	
90.0			2.60	

In all runs the initial concentration of sodium S-benzyl thiosulfate was 0.1 M.

increased.

Solvent deuterium isotope effects can be a useful tool in determining the mechanism of an acid catalyzed reaction in that they furnish information as to the timing of the proton transfer relative to the other processes taking place in a reaction. The observation that some reactions proceed faster in water than deuterium oxide indicates that the proton is transferred in the rate-determining step. If, on the other hand, an acid catalyzed reaction proceeds more rapidly in deuterium oxide than in water, evidence is furnished that the conjugate acid of the reactant is an intermediate in an equilibrium prior to the rate-determining step.

In the present work the rate of hydrolysis of sodium S-ethyl thiosulfate, XXVII, was measured in water and under the identical conditions in deuterium oxide. The results in Table X show that the hydrolysis of XXVII proceeds 1.4 times more rapidly in deuterium oxide than in water.

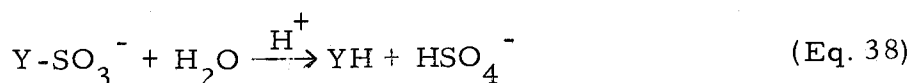
Table X. Kinetics of the Hydrolysis of Sodium S-Ethyl Thiosulfate in Water Deuterium Oxide at 95. 0°

Acid; Conc. M	Solvent	$k \times 10^4$ sec. ⁻¹
DCI; 0. 999	D ₂ O	1. 10
DCI; 0. 999	D ₂ O	1. 06
HCl; 0. 999	H ₂ O	0. 778
HCl; 0. 999	H ₂ O	0. 773
$k_{D_2O}/k_{H_2O} = 1.4$		

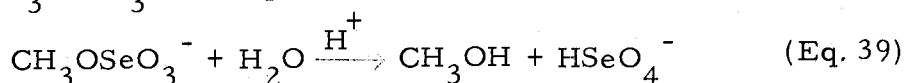
In all runs the initial concentration of sodium S-ethyl thiosulfate was 0. 10 M.

DISCUSSION

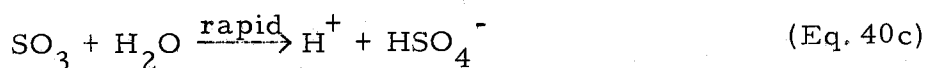
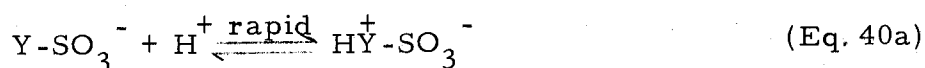
The Bunte salt hydrolysis is one of a series of hydrolysis reactions of the general form shown in Eq. 38. Some examples of



these are the hydrolyses of aryl and alkyl sulfates ($Y=ArO-$ and $RO-$), the hydrolyses of hydroxylaminetrisulfonate ($Y=-N(SO_3^-)OSO_3^{2-}$), hydroxylamine N, O- and N, N-disulfonate ($Y=-NHOSO_3^-$ and $-N(SO_3^-)OH$), and hydroxylamine N- and O-monosulfonate ($Y=-NHOH$ and $-ONH_2$). The acid hydrolysis of sodium methyl selenate, CH_3OSeO_3Na , (Eq. 39) is a related reaction involving

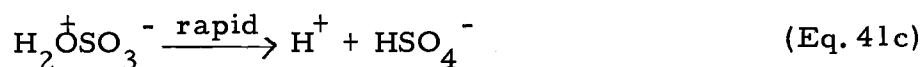
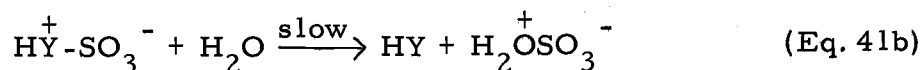
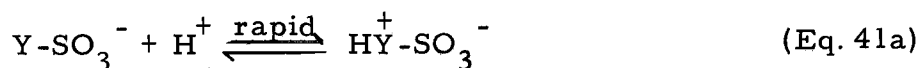


a selenium compound. For any of these acid-catalyzed hydrolyses one can a priori imagine several possible mechanisms. First, there is an A-1 mechanism, involving initial protonation of the Y-group of the substrate, followed by expulsion of HY from the intermediate zwitterion $HY^+-SO_3^-$ (Eq. 40). An A-1 mechanism involving initial



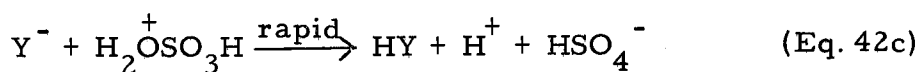
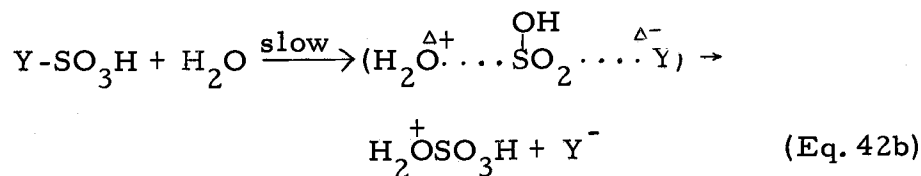
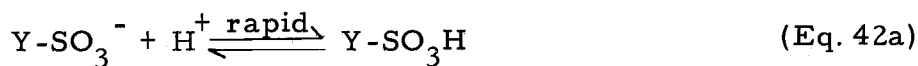
protonation on one of the oxygens of the sulfate sulfur can of course

be ruled out as a possibility, since, for the reasons outlined in the Introduction, heterolytic scission of the S-Y bond should occur much less readily in YSO_3H than in Y-SO_3^- . There are several types of possible A-2 mechanisms. The first, designated A-2a, involves initial protonation on Y; this converts -Y to the better leaving group $-\text{YH}^+$ which can then be more easily displaced by a nucleophile, which in this case would be water (Eq. 41). The other



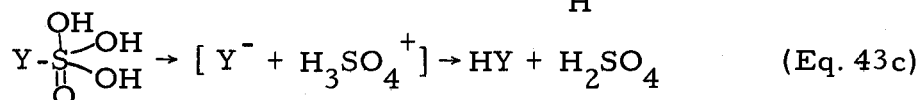
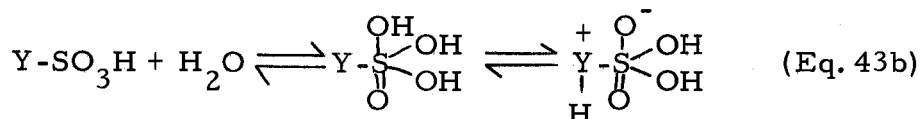
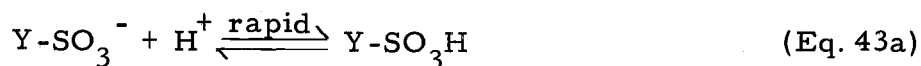
possible A-2 mechanisms involve initial protonation on oxygen.

This renders the sulfate sulfur more susceptible to nucleophilic attack. In the first of these mechanisms, designated as the A-2b mechanism (Eq. 42), this initial protonation is followed by nucleophilic displacement of Y^- by water. The other mechanism involving



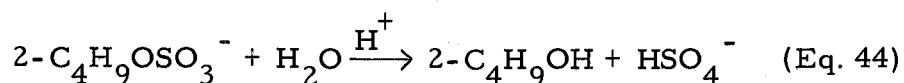
nucleophilic attack of water on $\text{Y-SO}_3\text{H}$, designated as an A-2b'

mechanism (Eq. 43), differs from the first in that an adduct with



water is formed. This adduct may decompose as in Eq. 43c or more likely, it may shift a proton to form the zwitterion $\overset{+}{Y}-\overset{\text{O}^-}{\underset{\text{H}}{\text{S}}}-\text{OH}$ which decomposes (Eq. 43d).

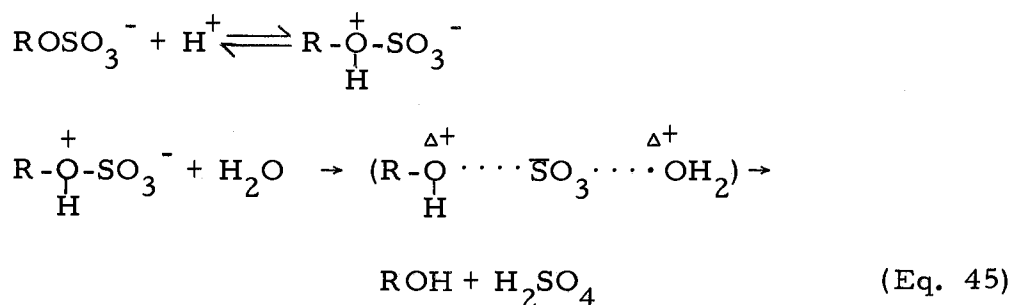
Experiments with optically active sodium 2-butyl sulfate have shown that the acid hydrolysis of alkyl sulfates (Eq. 44) generally



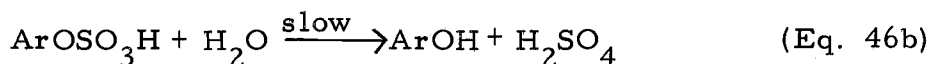
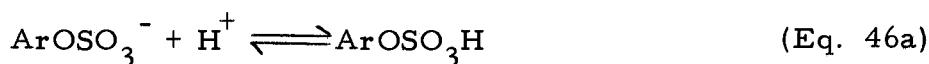
occurs with fission of the sulfur-oxygen bond (24). The rate of hydrolysis is increased as the percent of water in the solvent is decreased (23). The rate also appears to be first-order in the stoichiometric concentration of acid (23, 24). The entropy of activation for the hydrolysis of dehydroisoandrosterone sulfate is +11 e.u. in ethanol ($\Delta H^\ddagger = 29$ Kcal./mole) and +23 e.u. in tetrahydrofuran-6 percent water ($\Delta H^\ddagger = 30$ Kcal./mole) (23).

The mechanism of the sulfate hydrolysis is in somewhat of a confused state at present. Bernstein and Lieberman (23) feel that

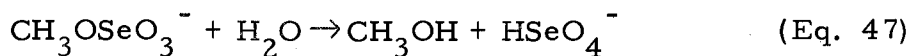
hydrolysis involves protonation on the alkyl oxygen followed by attack of water (Eq. 45). However, the rates of hydrolysis of



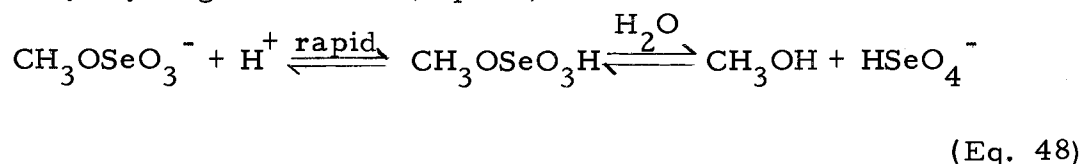
substituted aryl sulfates, which exhibit (21) the same acidity dependence as the alkyl sulfates, are accelerated by electron-withdrawing substituents in the same manner as those substituents enhance the acidity of the corresponding phenols (22). This latter fact would seem to suggest that the ArO- group has considerable anionic character in the rate-determining transition state. If the aryl and alkyl sulfates undergo acid hydrolysis by the same mechanism, and there seem no strong reasons a priori why they should not, the mechanism suggested by Berstein and Lieberman (23) is inconsistent with the substituent effect observed with the aryl sulfates. A mechanism consistent with this data would involve protonation on the sulfate group followed by attack of water, an A-2b mechanism (Eq. 46).



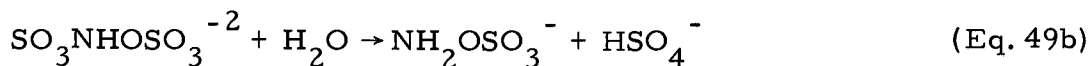
The acid hydrolysis of sodium methyl selenate (Eq. 47) occurs



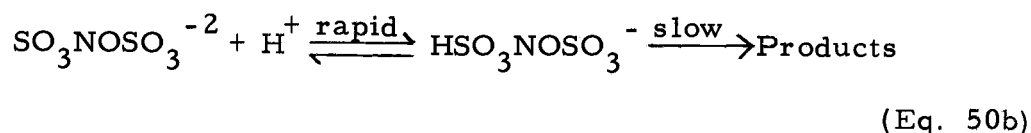
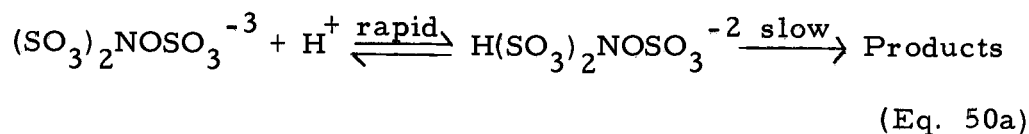
very readily in water (17). In dioxane-water mixtures the rate of hydrolysis increases as the dielectric constant of the medium is reduced. Unlike the acid hydrolysis of alkyl hydrogen sulfates, the entropy of activation is large and negative, -23 e.u., suggesting a bimolecular reaction and the activation energy is small, 17.6 Kcal./mole. The magnitude of the solvent isotope effect, $K_{\text{D}_2\text{O}}/K_{\text{H}_2\text{O}} = 1.36$, is in the range general for A-2 reactions (19). Plots of the logarithm of the first-order rate constant against the stoichiometric concentration of acid are linear with slopes ranging from 0.8 to 0.9, suggesting that water plays an important role in the rate-determining step (54). The above data led Bunton and Hendy (17) to suggest an A-2b mechanism involving attack of water upon the selenium atom of methyl hydrogen selenate (Eq. 48).



The hydroxylaminetrisulfonate (Eq. 49a) and hydroxylamine-N, O-disulfonate ions (Eq. 49b) appear to undergo acid hydrolysis by the same mechanism (26). Both reactions have a large solvent



isotope effect, $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 3.1$ and $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 2.6$, respectively, a large positive entropy of activation, $+11.2$ e. u. and $+14.9$ e. u., respectively, and their rates are correlated by the H_0 acidity function. This data seems most consistent with an A-1 mechanism (Eq. 50).

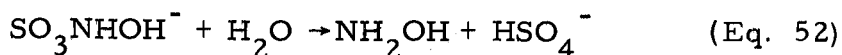


The acid hydrolyses of hydroxylamine-N,N-disulfonate and hydroxylamine-N-monosulfonate show striking differences (27). The hydrolysis of hydroxylamine-N,N-disulfonate (Eq. 51) resembles those in Eq. 50 with its positive entropy of activation, $+4$ e. u., and its



large solvent isotope effect, $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 3.1$. Its rate also follows the H_0 acidity function. Thus it too appears to hydrolyze by an A-1 mechanism.

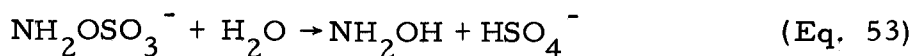
Hydroxylamine-N-monosulfonate (Eq. 52), on the other hand, has a rather large negative entropy of activation, -12 e. u., and the rate of hydrolysis follows the stoichiometric concentration of acid (27).



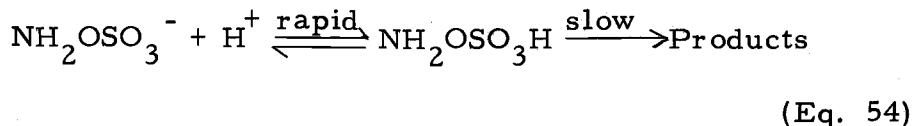
Both of these observations support an A-2 mechanism, yet, the

solvent isotope effect $k_{D_2O} = 2.86$, is in the range general for an A-1 mechanism (19). Candlin and Wilkins (27) feel that the entropy of activation and the acidity dependence of the rate firmly establish an A-2 mechanism for the acid hydrolysis of hydroxylamine-N-monosulfonate, but in view of the solvent isotope effect others might feel this conclusion debatable.

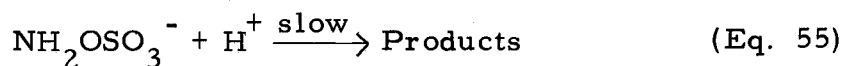
The O-monosulfonate of hydroxylamine (Eq. 53) hydrolyzes by



a mechanism different from any of the above compounds. O^{18} -studies show that like the other cases this hydrolysis also involves cleavage of the S-O bond. While the rate follows the H_o acidity function the reaction has a negative entropy of activation, -9 e. u. The most unique feature of this particular hydrolysis is the fact that it shows a primary kinetic isotope effect (20, 27), $k_{D_2O}/k_{H_2O} = 0.5$. Contrary to the opinion of Candlin and Wilkins (27), an A-1 mechanism involving a pre-equilibrium step followed by a rate-determining decomposition (Eq. 54) is ruled out as being inconsistent with the primary kinetic

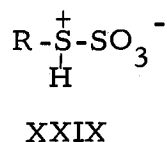


isotope effect. A mechanism consistent with the data is one involving the transfer of a proton in the rate-determining step, such as in Eq.



In the acid hydrolysis of Bunte salts we have seen from the work of Kice (41) that the rate of hydrolysis of XXVII shows an excellent correlation with the H_0 acidity function with slopes near 1.0, but that this effect of acid can be consistent with both A-1 and A-2 mechanisms.

Recent experiments in these laboratories³ measuring the rate of acid hydrolysis of substituted S-aryl thiosulfates show that the rate of hydrolysis is retarded as the substituent in the aromatic ring becomes more electron-withdrawing. These results indicate that there is a lower electron density on the ArS- group in the transition state than in the starting material. The zwitterion XXIX decomposing by either an A-1 (Eq. 40) or an A-2a (Eq. 41) mechanism would be



consistent with this observation. However, a mechanism in which an adduct with water is formed which then decomposes as in Eq. 43d is also consistent with this result.

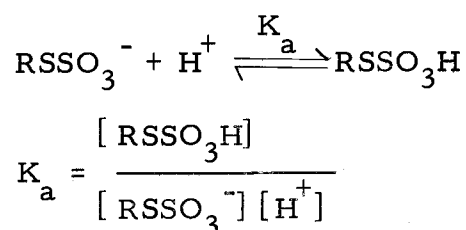
One cannot probably draw any very firm conclusions concerning the mechanism of the acid-catalyzed hydrolysis of Bunte salts

³Anderson, J. Unpublished research. Oregon State University, Corvallis, Oregon. 1965.

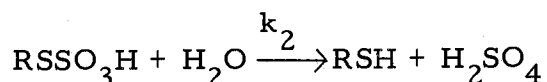
from the fact that the reaction exhibits a positive entropy of activation. For a given protonated substrate, decomposition by an A-1 mechanism will exhibit a more positive entropy of activation than will a bimolecular reaction of the same protonated substrate with water by an A-2 mechanism. The entropy of activation for the hydrolysis is the entropy of activation associated with the decomposition of the protonated substrate plus the entropy of protonation of the substrate. The difficulty in the present situation arises from the fact that the entropy of protonation of the Bunte salt is unknown. With our present state of knowledge of entropies of ionization, accurate estimation of the entropy of protonation of a Bunte salt seems impossible.

The significance of the effect of solvent upon the rate of hydrolysis of Bunte salts can best be seen by comparison with the hydrolysis of sodium methyl selenate. This latter compound almost certainly hydrolyzes by an A-2 mechanism (17). Upon changing from 40 to 60 percent dioxane the hydrolysis rate of sodium methyl selenate increases 1.6 fold (17). The same change in solvent increases the hydrolysis rate of the Bunte salt XXX by a factor of nearly six. Upon changing from 60 to 80 percent dioxane the hydrolysis rate for sodium methyl selenate increases 3.8 fold while the hydrolysis rate of XXX increases 21 fold. The rates of both hydrolyses might be expected to increase with increasing dioxane content of

the medium because increasing the percentage of dioxane will decrease the dissociation constants of the conjugate acids of both the Bunte salt and the selenate ester. In other words, K_a increases with increasing percent dioxane in the solvent. However, for an



A-2 mechanism this accelerating effect on the rate of hydrolysis resulting from the increase in K_a will in part be compensated for by a decreased rate for the reaction

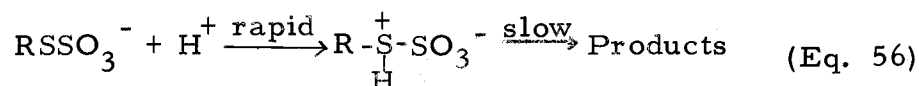


resulting from the fact that adding dioxane lowers the activity and concentration of water. One might therefore expect that an A-1 hydrolysis of a salt of the type in question would show a larger increase in rate with increasing dioxane content than would the corresponding A-2 hydrolysis.

Given the fact that the alkyl selenate hydrolysis is almost certainly an A-2 reaction, the significantly greater increase in rate with increasing dioxane content observed with the Bunte salt hydrolysis suggests that this latter reaction may be proceeding by an A-1 mechanism.

The effect of substituents on the rate of hydrolysis of aryl

thiosulfates is also compatible with an A-1 mechanism of the type shown in Eq. 56 for the Bunte salt hydrolyses.



At first glance the solvent isotope effect for the hydrolysis of XXVII, $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 1.4$, seems too low for an A-1 mechanism, since A-1 mechanisms are normally thought to have solvent isotope effects of 1.8 or greater. However we feel that this abnormality can be accounted for quite readily when one takes into consideration the fact that in XXIX the protonation occurs on sulfur.

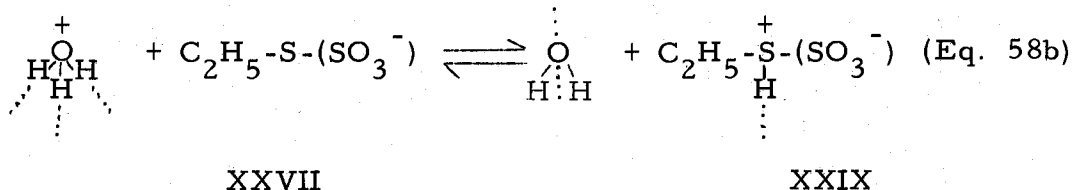
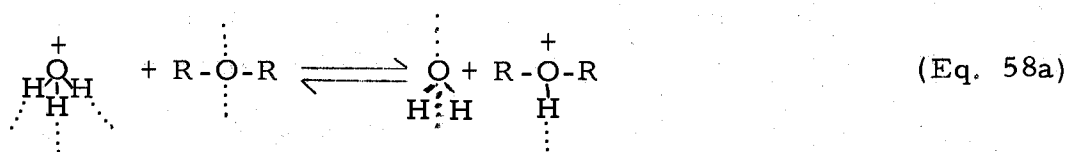
Bunton and Shiner (18, 19, 65) point out that deuterium oxide solvent isotope effects arise principally from changes in the zero-point energy between the reactants and the transition state which in turn are associated principally with the changes in the stretching frequencies associated with various bonds involving hydrogen atoms. The changes in vibrational frequencies for all hydrogens which will be influenced by the change from light to heavy water must be accounted for. This involves, besides all of the readily exchangeable hydrogens of the reactants and the transition state, those of any solvent molecules hydrogen bonded to either reactants and transition state. Although the exact number of water molecules hydrogen bonded to a Bunte salt and the vibrational stretching frequencies of their hydrogens are elusive quantities, one can quite likely obtain

some estimate of how the solvent isotope effect for an A-1 mechanism involving XXIX would compare with that normally observed by the calculations outlined in the succeeding paragraphs.

According to Bunton and Shiner (19) the kinetic isotope effect is related to the difference in the summation of the hydrogen stretching frequencies $\Sigma \nu_{\text{H}}$ and $\Sigma \nu'_{\text{H}}$ in the initial and transition states divided by the absolute temperature T . This relation is given in Eq. 57. Analogously to their method (18) for representing the

$$k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = \text{antilog} \frac{\Sigma \nu_{\text{H}} - \Sigma \nu'_{\text{H}}}{12.53 T} \quad (\text{Eq. 57})$$

protonation of ethers (Eq. 58a) we shall represent the protonation of a Bunte salt by Eq. 58b. The dotted lines in Eq. 58 represent



hydrogen bonding to and from solvent molecules and the parentheses is placed around the sulfate group because we are going to assume that any hydrogen bonds from solvent to it should remain approximately constant during protonation and can therefore, to a first approximation, be neglected. We will base our calculation on the protonated Bunte salt because we feel the structure of the transition

state should be fairly close to XXIX.

For H_3O^+ the average stretching frequency is 2900 cm.^{-1} and for H_2O a frequency of 3400 cm.^{-1} is assigned for each hydrogen and for each hydrogen bond accepted from a water molecule (18). For Eq. 58b a frequency of 3400 cm.^{-1} is added to the initial state for each hydrogen bond accepted by water in the final state, since a solvent-solvent bond must be broken to generate it. Finally, Bunton and Shiner (18) feel that since ethers have about the same basicity as water, the OH stretching frequency of a protonated ether should be about the same as the OH stretching frequency in H_3O^+ , 2900 cm.^{-1} . Obviously, the SH stretching frequency in XXIX will be considerably lower than 2900 cm.^{-1} since SH stretching frequencies are generally lower than the corresponding OH frequency (8, p. 350). Since we have no knowledge of the magnitude of the SH stretching frequency in XXIX let us assign a maximum value of 2600 cm.^{-1} , the stretching frequency for the SH bond in mercaptans, understanding that this is an upper limit.

Using these values then, we get for the initial and final states in Eq. 58b:

$$\Sigma \nu_{\text{H}} = 3(1900 \text{ cm.}^{-1}) + 2(3400 \text{ cm.}^{-1}) = 15,500 \text{ cm.}^{-1}$$

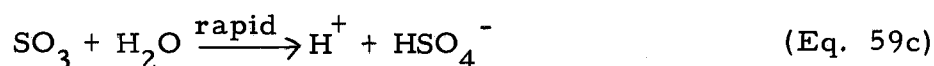
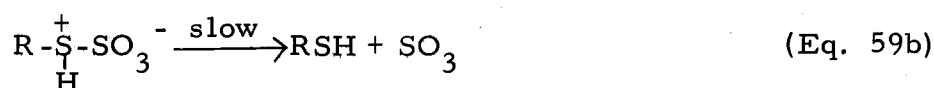
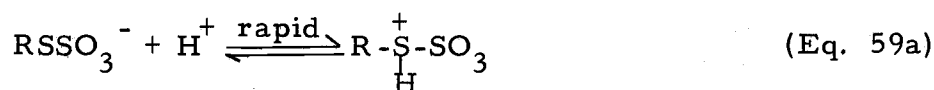
$$\Sigma \nu'_{\text{H}} = 4(3400 \text{ cm.}^{-1}) + (2600 \text{ cm.}^{-1}) = 16,300 \text{ cm.}^{-1}$$

Putting these values into Eq. 57 at a temperature of 368°K we get a

value $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 0.67$ or $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 1.49$.

This value of $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}}$, 1.49, estimated for the acid hydrolysis of a Bunte salt by an A-1 mechanism is a maximum value since decreasing the SH stretching frequency will decrease the solvent isotope effect to a value closer to the observed value of 1.4. Therefore, we feel that an A-1 mechanism for the acid hydrolysis of Bunte salts is perfectly consistent with the observed solvent isotope effect. In the present case the solvent isotope effect will be much smaller than those usually associated with A-1 mechanisms because protonation on sulfur gives a conjugate acid whose proton has a much lower stretching frequency than is observed for oxygen acids such as the conjugate acid of the ether in Eq. 58a.

Although, at the present time one cannot completely rule out an A-2 mechanism for the acid hydrolysis of Bunte salts, it certainly would seem that overall the experimental data are more consistent with an A-1 mechanism of the sort shown in Eq. 59. This mechanism is consistent with the correlation of rate with H_0 acidity function



(41), the effect of solvent polarity on rate and the large positive

entropy of activation. While the solvent isotope effect cannot be used to confirm an A-1 mechanism, we have just seen that it is entirely in accord with what might be expected for the mechanism represented in Eq. 59.

EXPERIMENTAL

Materials

Sodium S-Ethyl Thiosulfate.(XXVI). Sodium S-ethyl thiosulfate was prepared by the procedure used by Kice (41). Equal molar quantities of sodium thiosulfate and ethyl bromide were stirred together at room temperature in 20 percent ethanol-water until all of the organic halide dissolved. The solvent was removed under reduced pressure and the remaining solid was dissolved in hot ethanol, filtered and recrystallized twice from ethanol. The product was then recrystallized three times from water and dried in a vacuum desiccator over calcium chloride for two days at 0.1 mm.

Sodium S-Benzyl Thiosulfate. (XXX). Sodium S-benzyl thiosulfate was prepared according to the method given by Milligan and Swan (55). Equal molar quantities of benzyl bromide and sodium thiosulfate were mixed with an equal weight of 50 percent ethanol-water. The mixture was heated to boiling, filtered hot and allowed to cool. The solvent was removed under reduced pressure and the residue was extracted with boiling 95 percent ethanol. On cooling this extract the Bunte salt crystallized out. The salt was recrystallized twice from water and three times from ethanol-water mixtures. It was dried over calcium chloride in a vacuum desiccator at 0.1 mm.

Deuterium Chloride. (Carl Roth Karlsruhe, Germany) ca. 20 percent DCl in D₂O.

Deuterium Oxide. (Volk Radio-chemical Co.) 99.5 percent D₂O.

Solvents

Dioxane-Water Mixtures. Solutions of dioxane-water were made to 40, 60 and 80 percent dioxane by volume. The dioxane was purified as described in the Experimental of Section I. The normality of a 70 percent stock solution of reagent grade perchloric acid was determined by titration with standard base. An amount of this perchloric acid sufficient to give the resulting solution the desired acidity was weighed out. The amount of water in the perchloric acid was calculated and taken into account when calculating the volume of water to be added to the dioxane. The acidity of the resulting solutions was determined by titrating samples with 0.100 N base.

Deuterium Chloride in Deuterium Oxide. Ten grams of approximately 20 percent deuterium chloride were diluted to 26 ml. with deuterium oxide. Three one milliliter samples were taken and titrated with 0.100 N sodium hydroxide from a microburette. The resulting solution was determined to be 0.9985 N. The hydrochloric acid solution used for comparison was made up in the same manner with a resulting acidity of 0.999 N.

Procedures

Kinetics in Dioxane-Water Solutions. A weighed amount of XXX was dissolved in a measured volume of the desired dioxane-water mixture. The solution was then placed in the reaction vessel shown in Figure II section I, deaerated for 20 minutes with dry nitrogen and placed in a constant temperature bath. During the course of the reaction 4 ml. aliquots were removed and immediately added to 20 ml. of 50 percent ethanol-water. These solutions were then titrated with 0.1 N iodine solution. As in the kinetic studies of the sulfinyl sulfone decomposition (Section I) the first-order rate constant was calculated from plots of $\log (V - V_{\infty} / V_0 - V_{\infty})$ against time.

Kinetics in Water or Deuterium Oxide. Kinetic studies of the acid hydrolysis of sodium S-ethyl thiosulfate were carried out using exactly the same procedure employed by Kice (41). A 0.10 M solution of the Bunte salt was dissolved in 24 ml. of 0.999 N hydrochloric acid or deuteriochloric acid and placed in flask A of the kinetic apparatus shown in Figure V. After deaerating the solution for 15 minutes it was then placed in a constant temperature bath at 95.0°. The low boiling ethyl mercaptan is swept out from the reactor solution by a stream of pure anhydrous nitrogen, through the air condenser B, and into trap C. Trap C, submersed in an ice bath, contains an

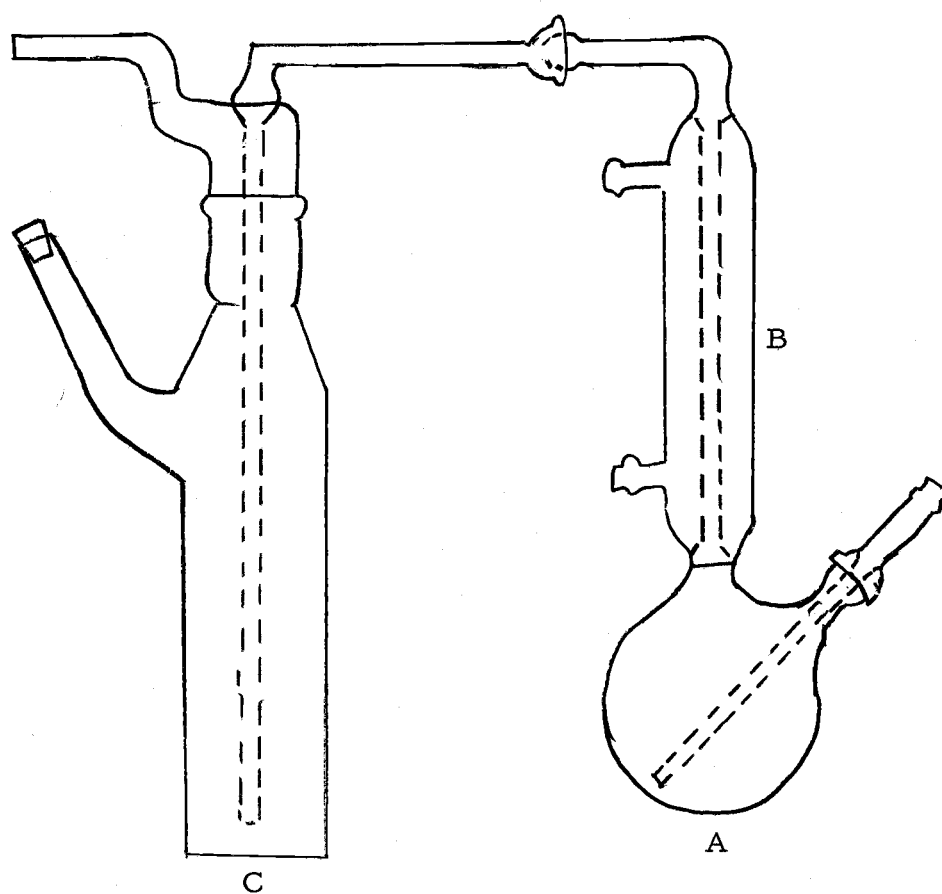


Figure V

aliquot of standard 0.1 N solution of iodine in potassium iodide diluted with an equal volume of ethanol. The time at which the first iodine aliquot became colorless was recorded, and a second aliquot of 0.1 N standard iodine solution was immediately added. This procedure was repeated until mercaptan evolution indicated that the hydrolysis was 93 percent complete at which time an excess of iodine solution was added. After the reaction had proceeded ten half lives the infinity value, V_{∞} , for the volume of iodine solution consumed was determined by back titration with standard sodium thiosulfate solution. The first-order rate constant was calculated from a plot of $\log (V - V_{\infty} / V_0 - V_{\infty})$ against time. The time at which the first iodine aliquot became colorless was taken as zero on the time scale.

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