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Sulfilimine. I. Synthesis and Formation Mechanism

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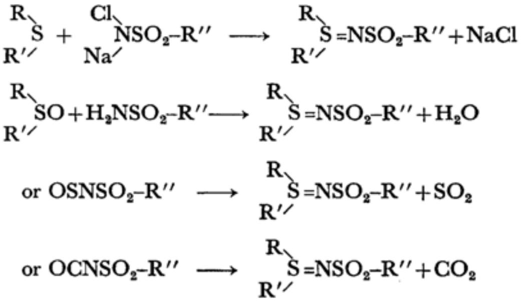
The kinetics of the reaction of sulfide and chloramine T was investigated. The reaction was very much affected by pH, and the rate reached the maximum at pH 5.5. The reaction was found to be facilitated by the substitution of an electron-releasing group in phenyl rings of aryl methyl sulfides. From these observations the rate-determining step appears to involve the formation of the sulfonium cation intermediate. From the mechanistic study of this reaction, an effective procedure for the synthesis of sulfilimine was devised.

N-Sulfonylsulfilimines have been known to be prepared either by treating the corresponding sulfides with *N*-sulfonyl-haloamide,[1] or by the reaction of the sulfoxides with sulfonamide[2] or sulfinylsulfonamide[3] or sulfonylisocyanate.[4] Among these, the first method is most commonly used.



$$\overset{R}{\underset{R'}{S}} + \overset{Cl}{\underset{Na}{N}}SO_2\text{-}R'' \longrightarrow \overset{R}{\underset{R'}{S}}{=}NSO_2\text{-}R'' + NaCl$$

$$\overset{R}{\underset{R'}{SO}} + H_2NSO_2\text{-}R'' \longrightarrow \overset{R}{\underset{R'}{S}}{=}NSO_2\text{-}R'' + H_2O$$

$$\text{or } OSNSO_2\text{-}R'' \longrightarrow \overset{R}{\underset{R'}{S}}{=}NSO_2\text{-}R'' + SO_2$$

$$\text{or } OCNSO_2\text{-}R'' \longrightarrow \overset{R}{\underset{R'}{S}}{=}NSO_2\text{-}R'' + CO_2$$

However, it is difficult to synthesize diarylsulfilimines by these methods, especially those bearing strong electron-withdrawing substituents such as halo or nitro groups. This may suggest that the formation of sulfilimine from sulfide and haloamide involves the initial slow step of halogenation of sulfide with active halogen, since the electron-withdrawing groups or substituents would hinder the formation of such a halogenated complex.

On the other hand, the similar reaction to synthesize sulfoxides from the sulfides and active halogen complex in aqueous media suggests that the initial halogenation is quite rapid and the subsequent nucleophilic attack of either acylate ion

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[1] F. G. Mann and W. J. Pope, *J. Chem. Soc.*, **121**, 1052 (1922).

[2] D. S. Tarbell and C. Weaver, *J. Am. Chem. Soc.*, **63**, 2939 (1941).

[3] G. Schulz and K. Kresze, *Angew. Chem.*, **75**, 1022 (1963).

[4] C. King, *J. Org. Chem.*, **25**, 352 (1960).

or water is the slow step of the reaction.[5]

Although there have been a few works[6] which deal with mechanisms of the reaction between sulfides and chloramine T, these data are not sufficient for considering the mechanism of the reaction in detail, since the reaction systems are too complicated and hence no well-defined kinetic study has been performed.

We have carried out an extensive kinetic investigation which includes the effect of pH and the substituent effect and found out that the reaction is very much dependent on the change of pH. Thus, when a condition is set at the pH giving the largest rate of this reaction, even diarysulfilimines bearing electron-withdrawing substituents can be readily prepared. This paper will describe a detailed account of the kinetic study and the application of the results to a useful synthetic procedure.

Results and Discussion

The Mechanism of the Reaction of Aryl Methyl Sulfides with Chloramine T. Aryl methyl sulfides and chloramine T were used for the kinetic experiments. The reaction was carried out in 60% aqueous methanol solution at a constant temperature and pH. The kinetic measurements for this reaction were carried out by following the increase of the absorbance due to I_3^- at 353 mμ in the spectrum, since it is reflected in the decrease of chloramine T which can oxidize potassium iodide to give free iodine in an acidic solution. In this case, a suitable acid to acidify the solution was acetic acid and not sulfuric acid or other strong mineral acids.

The reaction was found to follow the usual second order kinetic relationship nicely over the range of 0—80% reaction (Fig. 1).

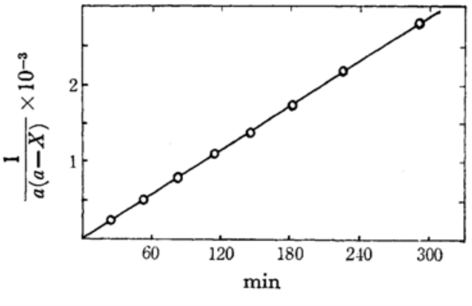

Fig. 1. Example of second order kinetics
a: the same initial concentration of methyl phenyl sulfide and chloramine T
x: a concentration of sulfilimine produced
reaction was carried out at 30°C and pH 8.61

The effect of pH on the apparent second-order rate constant K_{obs} was examined and the results are shown in Fig. 2. A plot of log K_{obs} vs. pH gives a straight line with a slope of −1.0 in the region between about pH 5.5 to pH 9, where the decrease of one pH unit results in the 10 fold increase of K_{obs} value.

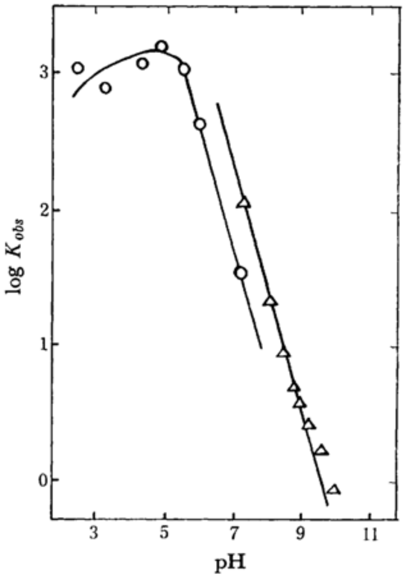

Fig. 2. The effect of pH on K_{obs}
○: at 15°C △: at 30°C

The effects of the p-substituents in the phenyl ring of the sulfides upon K_{obs} are shown in Fig. 3.

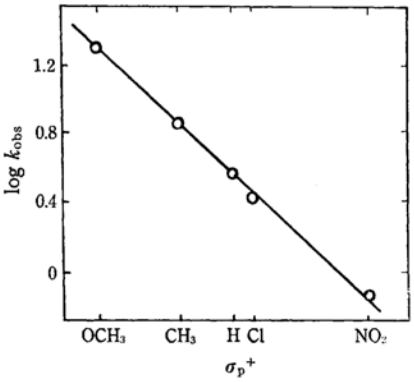

Fig. 3. The effects of the p-substituents in the aryl methyl sulfides on K_{obs}
temperature 30.0°C pH 9.07

A plot of log K_{obs} vs. σ_p^+ gives a straight line with a slope of −0.94 ($\rho = -0.94$). This seems to indicate that the formation of the chloro-sulfonium cation takes part in the rate-determining step of this reaction.

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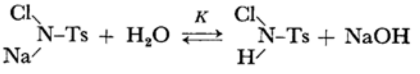
[5] T. Higuchi and K.-H. Gensch, *J. Am. Chem. Soc.*, **88**, 5486 (1966); W. Tagaki, M. Ochiai and S. Oae, *Tetrahedron Letters*, **58**, 6131 (1968).

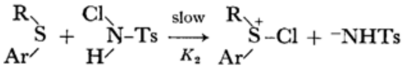
[6] J. Benes, *Collection Czech. Chem. Commun.*, **28**, 1171 (1963); A. Kucsman, I. Kapovits and M. Balla, *Tetrahedron*, **18**, 75 (1962).

Based on these observations, the following mechanism may be formulated for the reaction of sulfide with chloramine T.



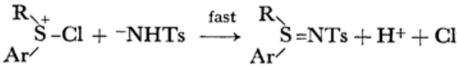
$$\underset{\mathrm{Na}}{\overset{\mathrm{Cl}}{\mathrm{N}}}\text{-Ts} + H_2O \overset{K}{\rightleftharpoons} \underset{\mathrm{H}}{\overset{\mathrm{Cl}}{\mathrm{N}}}\text{-Ts} + NaOH \qquad (1)$$

I II

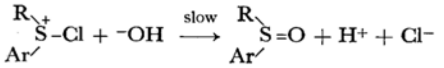


$$\underset{\mathrm{Ar}}{\overset{\mathrm{R}}{\mathrm{S}}} + \underset{\mathrm{H}}{\overset{\mathrm{Cl}}{\mathrm{N}}}\text{-Ts} \xrightarrow[K_2]{\text{slow}} \underset{\mathrm{Ar}}{\overset{\mathrm{R}}{\overset{+}{\mathrm{S}}}}\text{-Cl} + {}^{-}\mathrm{NHTs} \qquad (2)$$

II



$$\underset{\mathrm{Ar}}{\overset{\mathrm{R}}{\overset{+}{\mathrm{S}}}}\text{-Cl} + {}^{-}\mathrm{NHTs} \xrightarrow{\text{fast}} \underset{\mathrm{Ar}}{\overset{\mathrm{R}}{\mathrm{S}}}\text{=NTs} + H^+ + Cl^- \qquad (3)$$



$$\underset{\mathrm{Ar}}{\overset{\mathrm{R}}{\overset{+}{\mathrm{S}}}}\text{-Cl} + {}^{-}\mathrm{OH} \xrightarrow{\text{slow}} \underset{\mathrm{Ar}}{\overset{\mathrm{R}}{\mathrm{S}}}\text{=O} + H^+ + Cl^- \qquad (4)$$

Chloramine T (I) is presumed to be in the equilibrium with its free state (II) and sulfides are considered not to react with I but with II, since the rate of this reaction is very much facilitated by the addition of a weak acid, while I is not capable to liberate free iodine from potassium iodide in alkaline solution.

Meanwhile, in the reaction shown by Eq. (2), the sulfides that possess electron-richer S atoms would react more readily with (II), namely giving minus ρ value with substituted phenyl methyl sulfides, whereas, Eq. (3) involves the chlorosulfonium cation and requires an entirely opposite electronic effect for a facile formation of sulfilimines.

The small negative ρ values (-0.94) obtained from the overall rate constants appears to suggest that the rate determining step is the second step shown by Eq. 2.

Thus, the following rate equation may be formulated.

$$d[\text{Sulfilimine}]/dt = K_2[\text{II}][\text{Sulfide}]$$

$$\text{From Eq. (1), } [\text{II}] = \frac{K[\text{I}]}{[\text{OH}^-]} = K \times 10^{14-\text{pH}}[\text{I}]$$

$$\begin{aligned} d[\text{Sulfilimine}]/dt &= K_2[\text{II}][\text{Sulfide}] \\ &= K_2 \cdot K \cdot 10^{14-\text{pH}}[\text{I}][\text{Sulfide}] \\ &= K_{\text{obs}}[\text{I}][\text{Sulfide}] \end{aligned}$$

The use of aqueous media for a solvent of this reaction could lead to the formation of the by-product, sulfoxide, according to Eq. (4) and hence the addition of a larger amount of water into the system could give rise to the higher ratio of sulfoxide among the products.[6]

This was not the case, however, when the reaction was conducted in the presence of a small quantity of added acid; the time required for the reaction became very short and sulfilimines were formed nearly in quantitative yields. In the conventional procedure in which no weak acid is added, a considerable portion of sulfoxide is formed in the products. This is considered to be formed by the hydrolysis of sulfilimine once formed, since the formation of sulfilimine is quite slow and sulfilimine formed would be hydrolyzed slowly under the reaction conditions. These results show that the reaction shown by Eq. (3) is considerably faster than that of sulfoxide formation (Eq. (4)).

In Fig. 2, the plateau of the curve below about pH 5 is assumed to be due to the sudden change of the rate determining step of the reaction.

p-Toluenesulfonamide anion, ${}^{-}$NHTs, formed according to Eq. (2) begins to be protonated to form the corresponding sulfonamide in a low pH region and the chlorosulfonium cation formed would react not only with the sulfonamide, but also with the aqueous solvent media. As the corollary, the sole reaction product quantitatively obtained is sulfilimine at pH 6, but at pH 2 the yield of sulfilimine became 50% while sulfoxide is formed in the same 50% yield.

The rate of sulfoxide formation (Eq. (4)) is considered to be nearly equal to, or a little smaller than that of the halosulfonium cation formation in the reaction of sulfide with halogen in aqueous media, since it is known that the rate determining step of sulfoxide formation is the reaction of the halosulfonium cation with hydroxylic species.[5]

Synthetic Application. Since it has become clear that the formation of sulfilimine becomes very facile at around pH 5, we have devised a better reaction condition for facile syntheses of sulfilimines by the addition of a small amount of a weak acid, such as acetic acid.

Sulfilimine has been prepared usually by treating sulfide with an *N*-haloamide such as chloramine T in aqueous media with either methanol, acetone or some other water miscible solvents. However, the use of water often leads to the formation of a by-product sulfoxide, and sometimes makes it difficult to dissolve the sulfides such as methyl aryl sulfides and reduces the yields of products.

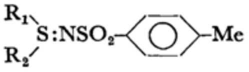
In order to overcome these difficulties, we used commercial methanol as the only solvent and increased the yield of *N*-sulfonyl-sulfilimines.

In general, dialkyl and alkyl aryl sulfides readily react with chloramine T. However, diaryl sulfides do not react with chloramine T under the same reaction condition. Moreover, when an electron-withdrawing group is introduced into either one of phenyl rings of the sulfides, the reaction does not proceed. However, when the reaction was carried out by adding a small amount of a weak acid such as acetic acid, even the diarylsulfilimines having nitro and halo groups were successfully obtained in high yields.

This method is quite effective, since the acid is acting on chloramine T to liberate the free chloramine T, which supplies an active chlorine to react readily with the lone electron pair of sulfides.

The yields and mps of sulfilimines are shown in Table 1.

TABLE 1. SULFILIMINES



$R_1R_2S{:}NSO_2\text{-}C_6H_4\text{-}Me$

R_1	R_2	Mp (°C)	Yield (%)	Method		Anal.		
						C, %	H, %	N, %
CH_3	CH_3	157—157.5	90	A				
$(CH_3)_2CH$	$(CH_3)_2CH$	117—118	95	A				
$CH_3(CH_2)_3$	$CH_3(CH_2)_3$	59—60	83	A				
$-(CH_2)_4-$		145—146	87	A				
$-(CH_2)_5-$		148—149	95	A				
CH_3	C_6H_5	129—130	90	A				
CH_3	p-$CH_3C_6H_4$	125—126	78	A				
CH_3	p-$CH_3C_6H_4$	125—126	95	B				
CH_3	p-$MeOC_6H_4$	144.5—145	74	A				
CH_3	p-ClC_6H_4	112—113	56	A	Found Calcd	51.48 51.30	4.24 4.27	4.15 4.27
CH_3	p-ClC_6H_4	112—113	95	B				
CH_3	p-$NO_2C_6H_4$	162—163	15[a]	A				
CH_3	p-$NO_2C_6H_4$	162—163	91	B				
CH_3CH_2	C_6H_5	97—98	82	A				
$(CH_3)_2CH$	C_6H_5	115—116	84	A				
$(CH_3)_3C$	C_6H_5	101 (decomp)	58	A				
$C_6H_5CH_2$	$C_6H_5CH_2$	190—191	80	A				
$C_6H_5CH_2$	C_6H_5	136—137	62	A				
$C_6H_5CH_2CH_2$	C_6H_5	137—138	66	A	Found Calcd	67.03 65.80	5.51 5.48	3.53 3.66
C_6H_5	C_6H_5	111—112	5[a]	A				
C_6H_5	C_6H_5	111—112	94	B				
C_6H_5	p-$CH_3C_6H_4$	96—98	58	B	Found Calcd	65.68 65.04	5.10 5.15	3.74 3.79
C_6H_5	p-ClC_6H_4	89.5—90.5	65	B	Found Calcd	58.60 58.54	3.96 4.11	3.46 3.59
C_6H_5	p-$NO_2C_6H_4$	148—149	59	B	Found Calcd	57.56 56.86	4.07 3.99	6.81 6.98
p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	130—132	68	A				

a) The product was separated by using chromatographic technique over silica-gel.

Experimental

Kinetic Procedure of the Mechanism of the Reaction of Aryl Methyl Sulfides with Chloramine T. The kinetic experiments were carried out while maintaining both the temperature (15±0.06, 30±0.08°C) and the pH constant using the following buffer solutions in 60% aqueous methanol media. After the reaction the pH of the solution was measured. Buffer solutions:

Potassium biphthalate-HCl (below pH 4), CH_3COOH-CH_3COONa (pH 4—6.5), KH_2PO_4-Na_2HPO_4 (pH 6.5—8.5), H_3BO_3, KCl-Na_2CO_3 (pH 8.5—10.5)

Both the sulfide and the chloramine T solutions preheated to the prescribed temperature were mixed quickly and the mixture was kept at a constant temperature during the kinetic experiments. An aliquot portion (1—2 *ml*) of the reaction mixture was taken up from time to time for 5—10 times and was quenched with 2 *ml* 1N KI. Then 5 *ml* 3N AcOH aqueous solution and the water was added to the prescribed volume.

Free iodine liberated from potassium iodide by the reaction with unchanged chloramine T is in the equilibrium with triiodide ion I_3^- with absorbance at 353 mμ was followed.

The concentrations of unreacted chloramine T were obtained by the following equation.

$$\text{Chloramine T} = \frac{A}{\varepsilon}$$

A: the absorbance at 353 mμ

ε: the molar extinction coefficient which was determined for using a known amount of chloramine T under the same condition.

Syntheses. The sulfides used were prepared by the general methods and purified either by distillation or recrystallization. The bps and mps of used sulfides are following:

di-methyl bp 37—38°C di-*i*-propyl bp 119—120°C, di-*n*-butyl bp 163—164°C, tetramethylene bp 119—120°C pentamethylene bp 140—141°C, methyl phenyl bp 84—85°C/15 mmHg methyl *p*-tolyl bp 81.5—82°C/7 mmHg, methyl *p*-methoxyphenyl bp 99°C/3 mmHg, methyl *p*-chlorophenyl bp 103—104°C/12 mmHg, methyl *p*-nitrophenyl mp 67—68°C, ethyl phenyl bp 85—86°C/

12 mmHg, iso-propyl phenyl bp 92—93°C/3 mmHg, *t*-butyl phenyl bp 96—97°C/15 mmHg, di-benzyl mp 49—50°C, benzyl phenyl mp 41—42°C, 2-phenylethyl phenyl bp 189—190°C/15 mmHg, di-phenyl bp 117—118°C/2 mmHg, phenyl *p*-tolyl bp 159—160°C/8 mmHg phenyl *p*-chlorophenyl bp 167—168°C/10 mmHg, phenyl *p*-nitrophenyl mp 55—56°C, di-*p*-methoxyphenyl mp 45—46°C. Sulfilimines were prepared from the corresponding sulfides and chloramine T by the following general methods (A) and (B).

(A): To 0.01 mol of sulfide in 20 m*l* of commercial methanol was added 0.011 mol of chloramine T in 20 m*l* of methanol at room temperature. The mixture was permitted to stand at 50°C for 1—5 hr and poured into a cold dilute sodium hydroxide solution. The precipitate was filtered, washed with water and recrystallized from methanol-water or acetone-hexane mixture.

(B): In 30 m*l* of methanol were dissolved 0.01 mol of sulfide and 0.011 mol of chloramine-T. To this solution was added dropwise 1.0 m*l* of acetic acid in 5 m*l* of methanol at room temperature. The mixture was allowed to stand at 50°C for 0.2—3 hr and poured into a cold dilute sodium hydroxide solution and a precipitate formed was filtered, then washed with water, Sometimes an oily product was extracted with two 30 m*l* portions of chloroform and the chloroform layer was washed with water, dried and the solvent removed. The residue was then washed with ether. Crude products were recrystallized from either acetone-hexane or methanol-water mixture.

The Reaction at a Low pH. Into a solution of methyl phenyl sulfide (0.001 mol) dissolved in 50 m*l* of methanol and 10 m*l* of 0.5N H_2SO_4 aq. chloramine T (0.0011 mol) dissolved in 10 m*l* of methanol was added and the reaction mixture (pH was about 2) was allowed to stand for 0.5 hr at room temperature, then poured into a dil-NaOH aq. solution. The products were extracted twice with each 30 m*l* portions of chloroform and the chloroform layer was washed with water, dried and the solvent removed. The composition of the products was calculated from the NMR spectra in which CH_3 on S atom of the sulfilimine and the sulfoxide and CH_3 in *p*-tolyl group give the chemical shifts of 2.84, 2.71 and 2.35 ppm respectively. The composition was found to be 50% sulfilimine and 50% sulfoxide.