

MECHANISM OF THE REACTION OF N-*p*-TOSYLSULPHILIMINE AND RELATED COMPOUNDS WITH THIOPHENOLATE ION

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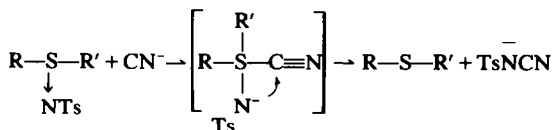
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Abstract—The reaction of alkyl aryl N-*p*-tosylsulphilimines with thiophenolate ion was found to afford quantitatively the sulphide that arises by an S_N2 like reaction on the carbon atom adjacent to the tri-valent sulphur atom. This reaction was also found to proceed smoothly with such compounds as sulphoxides and sulphones and sulphoximines. The kinetic study on the reaction between aryl methyl N-*p*-tosylsulphilimine with thiophenolate ion in DMF reveals that the reaction is of second order, namely, first order with respect to each thiophenolate ion and the sulphilimine. The enthalpy and entropy of activation for the reaction are ΔH[‡] = 17.8 kcal/mol and ΔS[‡] = -5.7 eu respectively. The

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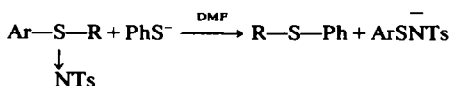
effect of substituents in the reaction, *p*-XC₆H₄S(NSO₂C₆H₄Y-*p*)CH₃ + *p*-ZC₆H₄SK is nicely correlated with Hammett σ values giving ρ_s = +2.4, ρ_v = +1.2 and ρ_c = -1.8 respectively. Meanwhile, a marked steric retardation by a bulky alkyl group in alkyl phenyl N-*p*-tosylsulphilimine is observed. Furthermore, from the stereochemical study of the reaction using an optically active *sec*-octyl phenyl N-*p*-tosylsulphilimine with thiophenolate ion it is concluded that the reaction proceeds via a typical S_N2 process on α-carbon atom attached to the tri-valent sulphur atom.

A study of nucleophilic substitution reaction on the tri-valent sulphur atom is quite interesting in comparison with that on the di- and the tetra-valent sulphur atoms or the sp³ carbon atom respectively.¹ Although considerable amounts of works on the substitution reaction at the tri-valent sulphur atom have been accumulated already, most of them were carried out in acidic media.² Recently, Cram *et al.* found that the alkaline hydrolysis of the aryl methyl N-*p*-tosylsulphilimines gave the corresponding sulphoxides.³ On the basis of kinetic and stereochemical results, they suggested that the reaction proceeds through the initial attack of hydroxide ion on sulphur atom affording a penta-valent sulphur compound (Sulphurane⁴) as an intermediate or transition state. Meanwhile, we have reported that the N-*p*-tosylsulphilimine reacts smoothly with cyanide ion in DMSO affording the corresponding sulphides.⁵ Based on the product analysis and the kinetic observation the reaction was suggested to proceed via the "addition-elimination" process on the sulphur atom as shown below.

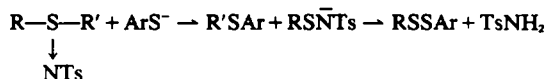


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SCHEME 1

Thus, all these observations indicate that the N-*p*-tosylsulphilimine is a good model to investigate the nature of nucleophilic substitution reactions at the tri-valent sulphur atom. In the nucleophilic substitution reaction at tri-valent sulphur atom, the formation of a tetra-coordinated penta-covalent sulphur compound or an intermediate with a phantom ligand of a lone electron pair has been postulated. In order to obtain further information on such nucleophilic substitution reactions on the tri-valent sulphur atom several substituted phenyl methyl N-*p*-tosylsulphilimines have been subjected to the reaction with thiophenolate ion, which is a softer and thus a better nucleophile than cyanide ion.⁶ However, unexpectedly the reaction gave the following interesting products which appear to be formed in the substitution reaction on the carbon atom adjacent to the tri-valent sulphur atom.



This paper will describe the detailed accounts of the results obtained on the reactions of N-*p*-tosylsulphilimine and the related compounds with thiophenolate ion, and discuss the scope and the mechanism of the reaction.

Table 1. Reaction of N-p-tosylsulphilimines with arylmercaptide ions^a

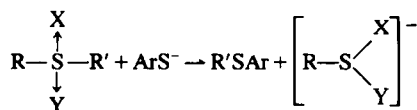
R	R'	Ar	Reaction condition			R'SAr	Products and yields (%)		TsNH ₂
			Solvent	°C	h		RSSAr	RSSR	
C ₆ H ₅	CH ₃	C ₆ H ₅	DMF	r.t.	5	quant.	78		82
C ₆ H ₅	CH ₃	C ₆ H ₅	DMSO	r.t.	5	quant.	81		80
C ₆ H ₅	CH ₃	C ₆ H ₅	MeOH	50	5	quant.	85		79
C ₆ H ₅	Et	<i>p</i> -CH ₃ C ₆ H ₄	DMF	r.t.	15	quant.	3	51	
C ₆ H ₅	<i>i</i> -Pr	<i>p</i> -CH ₃ C ₆ H ₄	DMF	50	15	quant.	trace	46	
C ₆ H ₅	<i>s</i> -Oct	<i>p</i> -CH ₃ C ₆ H ₄	DMF	50	15	quant.	trace	53	
C ₆ H ₅	CH ₃ Ph	<i>p</i> -CH ₃ C ₆ H ₄	DMF	r.t.	5	quant.			
C ₆ H ₅	CH ₂ CH ₂ Ph	<i>p</i> -CH ₃ C ₆ H ₄	DMF	r.t.	15	quant.			
C ₆ H ₅	C ₆ H ₅	<i>p</i> -CH ₃ C ₆ H ₄	DMF	50	5	—	RSR'(75)	(ArS) ₂ (86)	
CH ₃	CH ₃	C ₆ H ₅	DMF	100	2	75	RSR'(5)		97
Et	Et	C ₆ H ₅	DMF	100	2	66	RSR'(25)		97
—(CH ₂) ₄ —	—	C ₆ H ₅	DMF	r.t.	24	quant.			93
—(CH ₂) ₅ — ^b	—	C ₆ H ₅	DMF	100	12	12	15	30	73
—(CH ₂) ₆ — ^c	—	C ₆ H ₅	DMF	100	4	4	10	53	57

^a The reactions were carried out with 3 mmol of sulphilimines and 12 mmol of arylmercaptide ions in DMF (8 ml).

^b Besides these a liquid product was obtained, NMR suggested PhS(CH₂)₄SSPh (7.5 (m; 10H), 2.8 (m; 4H), 1.6 (m; 6H)).

^c A solid m.p. 54–55°C was isolated, probably (PhS(CH₂)₆S)₂.

Table 2. Reactions of the related compounds with arylmercaptide ions



R	R'	X	Y	Ar	Reaction °C	Condition h	Product (%) R'SAr
C ₆ H ₅	CH ₃	—	C(COOMe) ₂	C ₆ H ₅	r.t.	5	95
C ₆ H ₅	CH ₃	—	C(COOMe) ₂	<i>p</i> -CH ₃ C ₆ H ₄	r.t.	5	95
<i>p</i> -CH ₃ C ₆ H ₄	CH ₃	—	O	C ₆ H ₅	110	21	13
C ₆ H ₅	CH ₂ Ph	—	O	<i>p</i> -CH ₃ C ₆ H ₄	110	21	10
<i>p</i> -ClC ₆ H ₄	CH ₃	—	—	C ₆ H ₅	110	53	95
<i>p</i> -CH ₃ C ₆ H ₄	CH ₃	O	O	C ₆ H ₅	110	21	3
<i>p</i> -CH ₃ C ₆ H ₄	CH ₃	O	NH	C ₆ H ₅	110	21	17
<i>p</i> -ClC ₆ H ₄	CH ₃	O	NTs	C ₆ H ₅	110	21	
<i>p</i> -NO ₂ C ₆ H ₄	CH ₃	—	—	C ₆ H ₅	110	21	RSAr 13 ^a
<i>p</i> -NO ₂ C ₆ H ₄	CH ₃	—	O	C ₆ H ₅	110	21	59 ^a
<i>p</i> -NO ₂ C ₆ H ₄	CH ₃	O	NH	C ₆ H ₅	110	21	95

^a The yield of the sulphide (RSAr) was quantitative under more severe reaction condition (i.e. 150°C, 10 h).

RESULTS

Preparation of various N-p-tosylsulphilimines

The N-p-tosylsulphilimine can be readily prepared by the modified Mann–Pope reaction⁷ from the corresponding sulphides with sodium salt of N-chloro-p-tosylamide (chloramine-T) in the presence of a weak acid.

Reaction of N-p-tosylsulphilimine with arylmercaptide ion

The reaction was carried out by mixing a N-p-tosylsulphilimine with an excess of potassium arylmercaptide in DMF, DMSO or MeOH at room temperature. The products of the reaction and their yields obtained are summarized in Table 1.

The results reveal that alkyl aryl N-*p*-tosylsulphilimines always give in a quantitative yield the corresponding sulphides which arise by the substitution on the α -carbon atom of alkyl group attached to the tri-valent sulfur atom. Meanwhile, diphenyl N-*p*-tosylsulphilimine did not afford the corresponding sulphide, but the original sulphides that are presumed to be formed in a similar "addition-elimination" reaction on the tri-valent sulphur atom like in the reaction of the sulphilimine with cyanide ion.¹ Furthermore, dialkyl or cyclic analogues gave a mixture of these sulphides.

Incidentally a mixture of both symmetric and unsymmetric diaryl disulphides was obtained in the reaction of unsymmetric alkylaryl disulphide (R—SS—Ar) with an excess of arylmercaptide ion.

Reactions of related compounds with arylmercaptide ions

Similarly isoelectronic analogues of sulphilimine, i.e., sulphoxides and sulphur-ylides also react with arylmercaptide ions affording the same substituted products. Besides the above mentioned tri-valent compounds, even those containing di- or tri-valent sulphur atom such as alkyl aryl sulphide, sulphone and sulphoximine give the similar products. The products and their yields obtained are summarized in Table 2.

The results reveal that methyl *p*-tolylsulphonium bis(carbomethoxy) methylide give the α -carbon substituted product quantitatively at room temperature, while the sulphoxide, the sulphone and sulphoximine give the corresponding sulphide in low yields even though the reactions were carried out under prolonged heating at higher temperatures. Moreover, all of the alkyl *p*-nitrophenyl derivatives react with arylmercaptide ion in DMF, DMSO or methanol affording *p*-nitrophenyl phenyl sulphide in nearly quantitative yields. The reaction obviously proceeds through the nucleophilic substitution reaction on the carbon atom of aromatic ring and the reactivity falls in the following order, tetra- > tri- > di-valent sulphur compounds.

Kinetics and Hammett correlation

The kinetic study was carried out by means of gas-chromatography following the increase of the sulphide formed during the reaction. The rate constants were calculated with the usual second order kinetic equation, namely, rate = k_2 [sulphilimine] [ArS⁻]. As shown in Table 3 satisfactory rate constants were obtained with the second order kinetic equation at lower completion of the reaction (up to 30% completion), but gradually deviated from second order equation in the range of higher completion.

Thus, only the initial rate constants were used for the discussion of kinetics. The activation parameters of the reaction of methyl phenyl N-*p*-tosylsulphilimine with thiophenolate ion were calculated from the usual method and the values obtained are $\Delta H^\ddagger = 17.8$ kcal/mol and $\Delta S^\ddagger = -5.7$ e.u. respectively.

The second order rate constants of the reaction between the *para*-substituted aryl methyl N-*p*-tosylsulphilimine and *para*-substituted arylmercaptide ion are shown in Table 4.

A good Hammett correlation was observed for these *para*-substituted series by plotting the log(k_x/k_H) values against σ values and ρ values of +2.4 (x), +1.2 (y) and -1.8 (z) were obtained. Alkyl phenyl N-*p*-tosylsulphilimines with thiophenolate ion in DMF at 20.1°C and their relative rates for the reaction are shown in Table 5.

The second order rate constants of the tri-valent sulfur compounds, i.e., the sulphilimine, the sulphoxide and the sulphur-ylide, and their relative rates for the reaction in DMF at 20.10°C are shown in Table 6.

In the case of the *para*-chlorophenyl methyl sulphide, sulphoxide, sulphilimine, sulphone and sulphoximine the relative rates are summarized in Table 7.

Stereochemistry

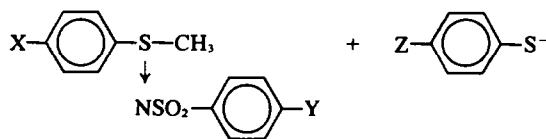
In order to clarify the mechanism of the reaction the stereochemical study was carried out with an

Table 3. Kinetic data (at 20.10 ± 0.02°C)

in DMF

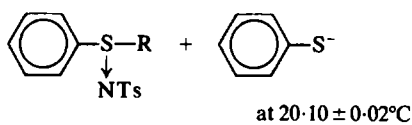
Sampling No.	Time (min)	PhSCH ₃ (%)	$k_2 \times 10^3$ (M ⁻¹ sec ⁻¹)
1	5	8.0	4.82
2	10	15.4	4.70
3	15	20.4	4.72
4	20	26.3	4.64
5	30	33.7	4.54
6	40	39.6	4.36
7	51	43.5	4.02

Table 4. Rate constants of the reaction of the *para*-substituted aryl methyl *N*-arylsulphonylsulphilimine with *para*-substituted arylmercaptide ions in DMF



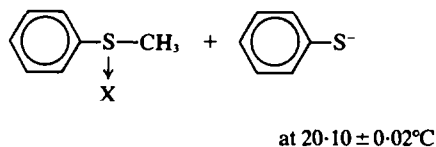
X	Y	Z	Temp. (°C)	$k_2 \times 10^2$ ($M^{-1} \text{sec}^{-1}$)	
CH ₃ O	CH ₃	H	20.10 ± 0.02	0.071	
CH ₃	CH ₃	H	20.10 ± 0.02	0.161	$\rho_x = +2.4$
H	CH ₃	H	20.10 ± 0.02	0.34	
Cl	CH ₃	H	20.10 ± 0.02	1.11	$\rho_y = +1.2$
H	CH ₃	H	10.60 ± 0.02	0.15	$\rho_z = -1.8$
H	CH ₃	H	20.10 ± 0.02	0.47	
H	CH ₃	H	30.50 ± 0.02	1.21	
H	H	H	20.10 ± 0.02	0.61	$\Delta H^\ddagger = 17.8 \text{ kcal/mol}$
H	Br	H	20.10 ± 0.02	0.96	$\Delta S^\ddagger = -5.7 \text{ e.u.}$
H	CH ₃	CH ₃	20.10 ± 0.02	0.40	
H	CH ₃	CH ₃	20.10 ± 0.02	0.183	
H	CH ₃	H	20.10 ± 0.02	0.116	

Table 5. The rate constants and relative rates of the reactions of alkyl phenyl *N*-*p*-tosylsulphilimine with thiophenolate ions in DMF



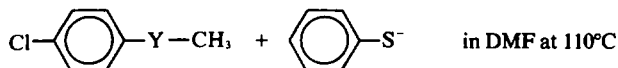
R	$k_2 \times 10^3$ ($M^{-1} \text{sec}^{-1}$)	$k_{\text{rel.}}$
Me	3.4	1
Et	0.2	0.06
<i>i</i> -Pr	0.01	0.003
benzyl	27	8

Table 6. The rate constants and relative rates of the reactions of tri-valent sulphur compounds with thiophenolate ions in DMF



X	$k_2 \times 10^2$ ($M^{-1} \text{sec}^{-1}$)	$k_{\text{rel.}}$
C(COOMe) ₂	7.8	23
NTs	0.34	1
O	0.001	10 ⁻⁴

Table 7. Relative rates of the reaction of related compounds with thiophenolate ions



Y	$k_{\text{rel.}}$	No. of lone electron pair ^a
	1.0	—
	0.2	3
	10 ⁴	2
	10 ⁻³	6
	10 ⁻³	5
	10 ⁵	1

^aThe number of lone electron pair existed at β -position of the reaction center.

optically active *sec*-octyl phenyl N-*p*-tosylsulphilimine which was prepared from *l*-(-)-phenyl *sec*-octyl sulphide and chloramine-T. The configurational assignment of the *sec*-octyl phenyl sulphide formed by the reaction of the corresponding sulphilimine with thiophenolate ion was carried out by changing it to the sulphone, since the optical rotation of the sulphone is larger than that of the sulphide and it can crystallize readily affording a pure compound. The procedure and the results obtained are illustrated in the following scheme, shown in Fig 1. *l*-(-)-*sec*-Octyl phenyl sulphide was treated with chloramine-T affording an optically active diastereoisomeric mixture of *l,l*- and *l,d*-sulphilimines. The diastereomers are separated readily by fractional recrystallization from ethanol four times. The maximum optical rotation $[\alpha]_D^{25}$ of + 235° was obtained for one diastereomer. The configurational assignment is now underway and will be published elsewhere. The reaction was carried out with the mixed diastereomers (one recrystallization from ethanol $[\alpha]_D^{25} = + 40.4^\circ$) with thiophenolate ion. After the reaction *sec*-octyl phenyl sulphide was isolated by column-chromatography, however, it was always accompanied by diphenyl disulphide which is hard to be separated by column-chromatography. Therefore the mixture was oxidized to the sulphone having $[\alpha]_D^{25}$ of + 11.1°. Similarly the starting sulphide (*l*-isomer) was oxidized

to the sulphone affording a maximum optical rotation $[\alpha]_D^{25}$ of - 12.5°. Obviously the stereochemical course of the reaction is a net inversion on the α -carbon atom and the optical purity is 88.2% which corresponds to 94.4% inversion.

DISCUSSION

Nucleophilic substitution on a sulphur atom, especially on di-valent sulphur atom has received considerable attention since Kharasch and Parker's proposition^{1a} concerning the valence bond expansion of the sulphur atom in the activated complex at the transition state or an intermediate formed in the reaction. Since that time, the discussions seem to have focussed mainly on whether or not such a valence bond expansion using vacant *d*-orbital is actually participating in the substitution on the sulphur atom, and in a number of references the formation of such an intermediate or so-called tetra-coordinated sulphur compound¹ has been described. Recently tetra-coordinated compounds have actually been isolated.⁹ Furthermore, recent works by Cram *et al.*^{3,4} and also by us^{5b, 10b} suggest that the sulphilimine is a good model to investigate the nature of the substitution reaction on the trivalent sulphur atom including the possible formation of tetra-coordinated intermediate. Previously, we found that N-*p*-tosylsulphilimines react with such nucleophiles as CN^{-5b} , $\text{Ph}_3\text{P}^{10b}$, N_3^{-5b} and RO^{-5b}

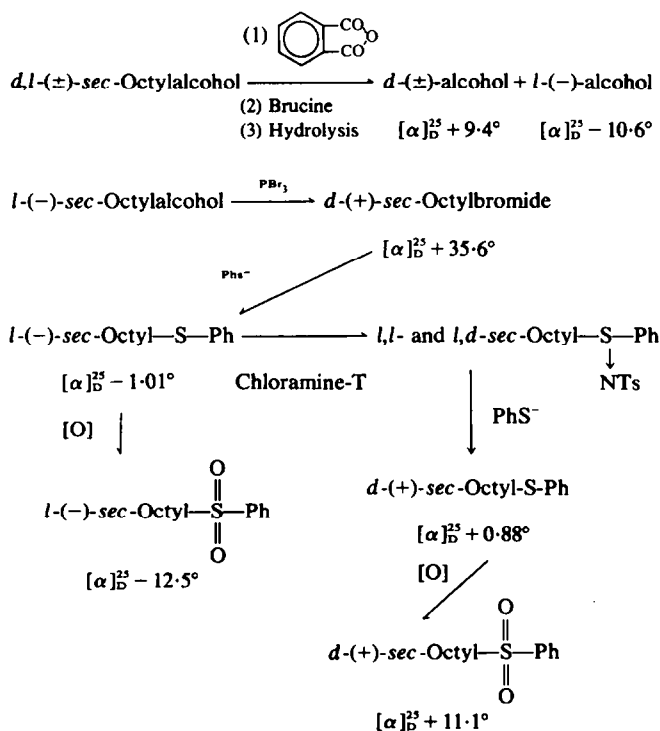
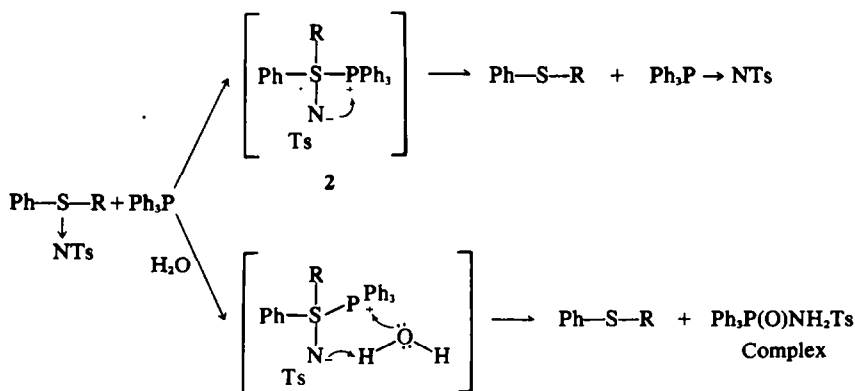


Fig 1. Stereochemistry of reaction of sulphilimine with thiophenolate ion.

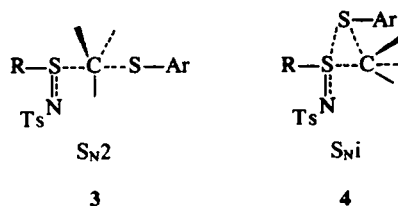
in DMSO, DMF or methanol to afford the corresponding substitution products. Especially in the case of CN^- , the reaction seems to proceed via an "addition-elimination" process on the tri-valent sulphur atom forming an incipient tetra-coordinated intermediate (1) which eventually collapses to the final products as shown in Scheme 1. Meanwhile, triphenylphosphine also gave the similar reduced product from the reaction with *N*-*p*-tosylsulphilimine. Here again the possible formation of a tetra-coordinated complex (2) was suggested on the basis of the kinetic results and the characteristic behavior in the presence of water^{10b} as shown in Scheme 2.



SCHEME 2

Since arylmercaptide ions are powerful nucleophiles toward the sulphur atom, they would attack the tri-valent sulphur atom of the sulphilimines. However, the result shown in Table 1, reveals that all the products seem to arise from the nucleophilic substitution on the α -carbon atom of alkyl or aryl group adjacent to the tri-valent sulphur atom. The results of the kinetic study with various substituted *N*-*p*-tosylsulphilimines in DMF are shown in Tables 4-5. The rate of the reaction can be calculated by the second order kinetic equation. The rate constants give a nice Hammett correlation with σ values and the following ρ values were obtained $\rho_x = +2.4$, $\rho_y = +1.2$ and $\rho_z = -1.8$ respectively. These ρ values and activation parameters suggest that the reaction proceeds via $\text{S}_{\text{N}}2$ process, namely, the nucleophilic attack of mercaptide ion at the carbon atom adjacent to the tri-valent sulphur atom ($\text{S}_{\text{N}}2$ on C, 3). However, another alternative path involving the initial attack of PhS^- on tri-valent sulphur atom followed with the intramolecular migration of PhS^- from S to C (S_{Ni} -like, 4) is also conceivable in view of the results with cyanide ion or triphenylphosphine.¹¹

The choice between these two was attained by the investigation of the stereochemistry of the reaction, namely, when the optically active *sec*-octyl phenyl *N*-*p*-tosylsulphilimine was subjected to the



reaction. If the reaction proceeds via $\text{S}_{\text{N}}2$ process on the α -carbon atom, the sulphide obtained should be of inverted configuration, while the initial attack is on S (S_{Ni} -like), the retention of the sulphide should be the stereochemical course. The results

clearly indicate that the configuration of the sulphide formed from the reaction was of inverted (nearly completely), thus supporting that the reaction proceeds through a typical $\text{S}_{\text{N}}2$ process on the α -carbon atom of alkyl group attached to the trivalent sulphur atom.

Steric effect due to alkyl group

In Table 8, the relative rate of various reaction including a few typical $\text{S}_{\text{N}}2$ type substitutions both on sp^3 carbon atom and the tri-valent sulphur atom. Therefore, as far as the steric effect due to alkyl groups is concerned, the reaction appears to proceed via the transition state (3).

Comparison of the reactivity between other sulphur compounds

As shown in Table 2, sulphides, sulphoxides and sulphones also gave the corresponding sulphides when they are treated with thiophenolate ion. The relative reactivities between these three compounds are markedly different as shown in Table 8, i.e., $-\text{S}- : -\text{SO}- : -\text{SO}_2- = 1 : 0.2 : 10^{-3}$. The sulphone is remarkably unreactive as compared with the corresponding sulphide or sulphoxide. Meanwhile, the relative rates among these trivalent sulphur compounds, sulphoxide, sulphilimine and sulphur-ylides as shown in Tables 6 and 7, fall in the

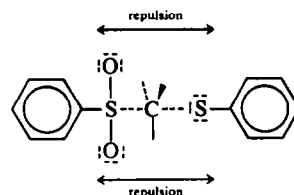
Table 8. Steric effect due to alkyl group

Reaction	R	Me	Et	<i>i</i> -Pr	
RBr + EtONa ¹³		1.0	0.05	0.002	S _N 2—C
RI + LiBr ¹⁴		1.0	0.05	0.001	S _N 2—C
Ar—S—R ↓ NTs	+ CN ^{-15b}	1.0	0.1	0.06	S _N 2—S
Tol—S—R ↓ O	+ HCl ¹⁵	1.0	0.26	0.08	S _N 2—S
Ar—S—R ↓ NTs	+ PhS ⁻	1.0	0.06	0.003	Present reaction

following order, 1:10⁴:10⁵, respectively. If the above reactions obey the simple S_N2 mechanism, it is necessarily to explain the large rate difference between —S— and —SO₂— groups, and even these in the series of tri-valent sulphur analogues. Generally speaking in the S_N2 reaction on the carbon atom the reactivity depends on the structure of the substrate or the solvent, namely, electronic, steric and field effects of substituents and the C—S bonds strength. The effect of electronic stability of the leaving group (*pKa*) cannot explain the reactivity of them shown in Table 8, because according to the ease of leaving group the stronger the acidity of the leaving group, the faster the S_N2 reaction and the reactivity should fall in the following order, —SO₂— > —SO— > —S—. Recently the C—S bond dissociation energies of the sulphide, sulphoxide and sulphone were determined by Mackel¹⁶ as shown in Table 9.

These values suggest that the C—S bond of the sulphone should be dissociated more preferentially than that of the sulphoxide. However, the orders of their reactivities observed in the present reaction decrease as in the following order, —S— > —SO— > —SO₂—. Recently, Bordwell *et al.* reported the S_N2 reaction of the following compounds, PhS(O)_nCH₂X + KI—(n = 0, 1, 2).¹⁷ In these series, they found that the reactivity of the compounds falls in the following order, —S— > —SO— > —SO₂—, and as an explanation of the large steric effect by the sulphonyl oxygen was suggested to prevent the access of the nucleophile like in the case of *neo*-pentyl group. Our result can be explained at least partly by the steric effect of the sulphonyl or sulphanyl group. However, it is difficult to explain the large rate difference between sulphilimine or sulphur-ylide and sulphoxide. As one of the probable explanations, the field effect due to lone electron pair repulsion between oxygen

or nitrogen and PhS⁻ may be considered to play an important role in this reaction. According to the above assumption, the number of lone electron pair would determine the reactivity of the compounds.



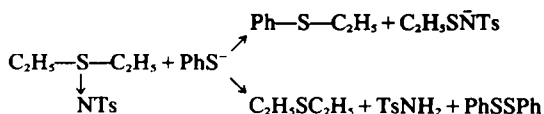
As shown in Table 8, there is a good correlation between the number of lone electron pair and their relative rate constants except the sulphide. Therefore, these lone electron pairs may form the negative screen around the reaction center thus preventing the approach of mercaptide ion toward the carbon atom as shown below.

Reaction of diaryl or cyclic sulphilimine with thiophenolate ion

Most N-p-tosylsulphilimines were found to react with RS⁻ to give the corresponding sulphide which appears to be formed by the substitution on the α -carbon atom. However, in the case of diaryl or tetramethylene N-p-tosylsulphilimines the product obtained is the original sulphide in nearly quantitative yield, suggesting that the mechanism of these reactions are similar to the nucleophilic attack on sulphur like in the case with CN⁻ and Ph₃P. Furthermore, a particularly interesting observation is that 6- or 7-membered cyclic and dialkyl N-p-tosylsulphilimines, especially diethyl N-p-tosylsulphilimine which is the open chain analogue of tetramethylene N-p-tosylsulphilimine gave both types of sulphides concurrently as shown in Scheme 3.

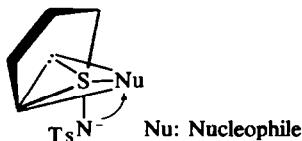
Table 9. Dissociation energies of C—S bond

C—S Bond	CH ₃ —SCH ₃	CH ₃ —SOCH ₃	CH ₃ —SO ₂ CH ₃
D.E. (kcal/mol)	72 ± 5	50.3	62 ± 3



SCHEME 3

An enormous reactivity of a five-membered cyclic *N-p*-tosylsulphilimine toward nucleophiles is also observed in the reaction with CN^- or Ph_3P . In the case of the five-membered cyclic compounds containing sulphur or phosphorus atom,²² the nucleophiles attack preferentially on sulphur or phosphorus atom and leads to the large rate enhancement as compared with 6- or 7-membered or the open chain compounds, since sulphur or phosphorus atom may expand the orbital to form a trigonal-bipyramidal intermediate or transition state in where the 5-membered compound can occupy the axial-equatorial position thus fixing the structure more preferentially. Therefore, with these cyclic compounds thiophenolate ion attacks on sulphur atom more preferentially than carbon atom, thus giving rise to the penta-valent intermediate from which the reduction takes place to give the original sulphide as shown below.



EXPERIMENTAL

Materials. Sulphilimines: All the *N-p*-tosylsulphilimines used were prepared by the usual method,⁷ by treatment of the corresponding sulphides with chloramine-T (sodium salt of *N*-chloro-*p*-toluenesulphonamide) in methanol solution. The m.p., IR and NMR spectra of the *N-p*-tosylsulphilimines are all identical to those prepared earlier.

Sulphur-ylides (sulphonium bis(carbomethoxy)methylide): The sulphonium bis((carbomethoxy)methylides were synthesized according to the procedure reported earlier.¹⁸

Sulphoxides, sulphones and sulfoximines: The sulphoxides¹⁹ and sulphones²⁰ were prepared by oxidation of the corresponding sulphides by known method.²¹ The sulfoximines were prepared by treatment of the corresponding sulphoxides with HN_3 .²¹

Arylmercaptide: All the arylmercaptides were prepared by the usual procedure, by just adding potassium hydroxide into the corresponding arylmercaptans dissolved in benzene-methanol soln. They were recrystallized from benzene twice and dried before use.

Solvents: All the solvents were purified by the usual method.

Preparation of optically active *sec*-octyl phenyl *N-p*-tosylsulphilimine. *l*-(-)-*sec*-Octyl phenyl sulphide: The sulphide was prepared according to the known method from *d*-(+)-*sec*-octyl bromide and thiophenolate in MeOH. The sulphide, b.p. 120°C/5 mm Hg, was identified from spectroscopic analysis. Yield was 74%.

l-(-)-*sec*-Octyl(-) and (*d*)-phenyl *N-p*-tosylsulphilimine: *sec*-Octyl phenyl sulphide (1 g) was treated with 1.8 g of chloramine-T in EtOH at room temp. The EtOH soln was poured into ice-water. The precipitates were filtered and dried. Yield was 1.8 g (92%), m.p. 106–107°C (recryst. from EtOH), $[\alpha]_D^{25} = +40.4^\circ$. This sulphilimine is a diastereomers mixture. The *l,l*- and *l,d*-ratio is almost 50:50 which was determined from the NMR peak due to phenyl proton. The sulphilimine was recrystallized 4 times from EtOH and gave a max. rotation $[\alpha]_D^{25} + 235^\circ$. The IR and NMR spectrum suggest *l,l*- or *l,d*-isomer, but the configuration around sulphur atom was not determined in the present experiment.

Reaction of *sec*-octyl phenyl *N-p*-tosylsulphilimine with thiophenolate ion: The reaction was carried out like the other sulphilimines. The title sulphilimine (1 g) was treated with $\text{PhS}^- \text{K}^+$ (1 g) to give the mixture (1:1 g) of diphenyl disulphide and *sec*-octyl phenyl sulphide. The GLC analysis indicated the mixture to be considered from 1:1:1 (molar ratio; sulphide:disulphide). Therefore the calculated yield of the sulphide was 0.52 g (92%), $[\alpha]_D^{25} + 0.88^\circ$ (c:5, CH_3OH).

sec-Octyl phenyl sulphone: (a) *l*-(-)-*sec*-Octyl phenyl sulphide (0.2 g) was oxidized with H_2O_2 in acetic acid soln. The yield was 0.19 g (83%), m.p. 46.5–47.5°C. Recrystallization from *n*-hexane twice gave a max. rotation $[\alpha]_D^{25} - 12.5^\circ$ (c:1, CH_3OH). (b) The same sulphide (*d*-isomer) obtained from the above reaction was treated similarly afforded 76% yield of the sulphone, $[\alpha]_D^{25} - 12.0^\circ$ (c:1, CH_3OH).

Reaction of the *N-p*-tosylsulphilimine with arylmercaptide ions. A typical run is as follows: Methyl phenyl *N-p*-tosylsulphilimine (3 mmol) and potassium thiophenolate (12 mmol) were dissolved into 8 ml of DMF in a sealed tube to avoid moisture and CO_2 in the air. The tube was shaken vigorously for a while and kept standing for 5 h at room temp. After the reaction, the tube was broken and the content was poured into 30 ml of ice cold water. The soln was acidified slightly with 2*N*-aqueous HCl soln. The products were extracted with chloroform. The chloroform soln was evaporated and the residue was passed through a chromatographic column packed with silica gel. The products separated were methyl phenyl sulphide, diphenyl disulphide and *p*-tosylamide. All those products were similar gas-chromatographic behaviors with those of the authentic samples.

Reaction of diphenyl or tetramethylene *N-p*-tosylsulphilimine with arylmercaptide ions. A typical run is as follows: A crystalline potassium *p*-tolylmercaptide (12 mmol) was added into a DMF soln of diphenyl or tetramethylene *N-p*-tosylsulphilimine (3 mmol) in a sealed tube. The tube was heated in an oil bath of 50°C for 5 h. Then the products were isolated and identified by the same method as described above.

The reaction of the related compounds with arylmercaptide ions. A typical run is as follows: A mixture of 3 mmol of methyl *p*-tolyl sulphoxide and 10 mmol of potassium thiophenolate was dissolved in 8 ml of DMF, and heated for 21 h at 110°C. Then the products were isolated and identified by the same method as described above.

Kinetics. A typical kinetic procedure is as follows: A reaction apparatus having two side arms was used. The DMF solutions of $\text{PhS}^- \text{K}^+$ and the sulphilimine were prepared and placed separately into the arms of the flask before mixing. The concentration of the components were 0.0625 mol/l of the sulphilimine and $\text{PhS}^- \text{K}^+$ respectively.

To this solution was added 0.02 mol/l methyl *p*-tolyl sulphide as an internal standard. The solution was pre-heated at a constant temperature before mixing. Then the two solutions were mixed and from this solution an aliquot (0.5 ml) of the sample was taken out with 1 ml syringe at constant time intervals. The soln was quenched immediately with 6 ml of water in an ampoule. After adding 0.5 ml of *n*-hexane it was shaken vigorously for a while. Then the *n*-hexane layer was separated and ca 5 μ l of it was injected directly into a column of gas-chromatography. The gas-chromatography was carried out at the following condition; column, diethyleneglycol succinate polyester on Celite, 1 m length, 3 mm i.d., stainless tube, temperature; 100°C, H₂-flow; 60 ml/min. The rate constants of the reaction were calculated by the well known 2nd order kinetic equation, where *a* is the initial concentration of the sulphilimine or thiophenolate ion and *x* is calculated from the relative peak-area of methyl phenyl sulphide and methyl *p*-tolyl sulphide (internal standard) using a calibration curve prepared in advance. Thus, each *x* means the amount of methyl phenyl sulphide formed at the time. The kinetics of other sulphilimines and related compounds were carried out as described above except changing the internal standard each time. The activation parameters were calculated as usual and the Hammett plots were drawn against σ values.

$$k_2 = \frac{x}{a(a-x)t}$$

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