Catalytic Reduction of Sulfoxide by Bromine–Hydrogen Bromide System

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A small amount of hydrogen halides or halogens was found to catalyze the decomposition of dimethyl sulfoxide (DMSO), affording dimethyl sulfide (DMS) and other oxidized products. Of the halides or halogens, either bromine or hydrogen bromide is the most effective. DMSO decomposes until it is completely consumed. This catalytic decomposition takes place with other sulfoxides such as diethyl or tetramethylene sulfoxide but sluggishly with alkyl aryl or diaryl sulfoxides. The reaction with bromine apparently proceeds *via* the initial α-bromination of DMSO to afford α-bromomethyl methyl sulfoxide which is oxidized by (Kornblum Reaction) to afford such products as formaldehyde, methanesulfonic acid, and hydrogen bromide. These consecutive reactions form a process of "Oxidation-Reduction Cycle" between bromine-hydrogen bromide and DMSO–DMS. The effects of salts and DMS on the rate of decomposition are discussed.

Recently, halide ions were found to catalyze the Stevens-type rearrangement of *S*-alkyl *S*-phenyl *N*-*p*-tosylsulfilimine in DMSO or *N*,*N*-dimethylformamide.[1] However, when DMSO was used as a solvent, an unexpected reduction of DMSO was observed besides the above rearrangement. The rate and amount of reduction vary with the halide ion. The catalyzed reduction of DMSO was attained most effectively with bromide ion, while the yield of dimethyl sulfide did not depend upon the amount of sulfilimide and bromide ion used. Reduction did not proceed in the absence of either the sulfilimine or bromide ion. These observations seem to indicate that the reduction is "triggered" by some species which is formed as a transient intermediate in the initial reaction of the sulfilimine and bromide ion (SB-System). A trapping experiment with a nucleophilic olefin confirmed that molecular bromine is formed during the course of reaction of the sulfilimine with bromide ion. Thus, the reduction is considered to be catalyzed by the molecular bromine formed during the course of reaction. This is supported by the fact that a drop of bromine or aqueous hydrobromic acid solution is enough to reduce DMSO to DMS completely upon heating. This catalytic reduction also takes place with other sulfoxides such as diethyl and tetramethylene sulfoxides. Although the reduction of sulfoxides with other acids has been reported,[2] this is the most facile and convenient catalytic reduction of sulfoxides.

This paper describes detailed observations on this new catalytic reduction of the sulfoxide triggered by the reaction of the sulfilimine with bromide ion and the implication of the reaction.

Results and Discussion

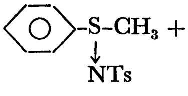
Reaction of N-p-*Tosylsulfilimines with Halide Ion in DMSO.* The reactions of *S*-methyl *S*-phenyl *N*-*p*-tosylsulfilimine with lithium halides were carried out in DMSO at 110 °C for 5 h. The products and yields obtained are summarized in Table 1.

In the case of bromide ion (SB-System) the reaction was apparently quite different from others (chloride ion or iodide ion), a large amount of dimethyl sulfide being obtained. The reaction with iodide ion gave a small amount of molecular iodine. In order to clarify the nature of this abnormal reaction with bromide ion, the yield of dimethyl sulfide was examined by changing the concentration of the bromide ion in DMSO. The results are given in Table 2.

Even though the total yield of dimethyl sulfide calculated from the amount of the SB-System markedly depends upon the initial concentration of the SB-System, the net yields of dimethyl sulfide calculated from the amount of DMSO used always remain at *ca.* 55%. During the course of reaction, about a half molar amount of DMSO used was reduced to the sulfide until DMSO was consumed. This suggests that the SB-System acts only as a "trigger" in the reduction of DMSO, and apparently a certain active species is generated from the SB-System during the course of reduction.

In order to understand the mechanism of the reaction with SB-System and the active species involved, the effect of structure of the sulfilimine on this reaction

Table 1. Reaction of sulfilimine with halide ion



$C_6H_5\text{-}\underset{\substack{\downarrow\\ NTs}}{S}\text{-}CH_3$ + LiX; X = Cl, Br or I

(Sulfilimine/LiX = 1/4; molar ratio)

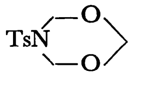
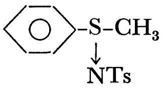
X	Products and Yields (%)			
	$TsNHCH_3$	PhSSPh	CH_3SCH_3	Others
Cl	93	88	0	—
Br	43	43	1400	 (34), $(CH_2O)_n$ (12)
I	71	62	30	I_2 (15)

TABLE 2. CONCENTRATION DEPENDENCY OF THE SB-SYSTEM

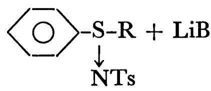


+ LiBr (SB-System)

Molar ratio (SB-System/DMSO)		0.01	0.05	0.25
Yield of DMS (%)	a)	615	1166	2420
	b)	55	53	56

a) Calculated from the amount of the SB-System.
b) Conversion percentage for DMSO.

TABLE 3. EFFECT OF THE STRUCTURE OF THE SULFILIMINE

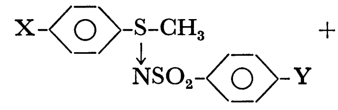


+ LiBr + DMSO; SI^b)/LiBr = 1/4, molar ratio

R	Me	Et	*i*-Pr	$PhCH_2$	Ph
k_{rel}[a]	1.0	0.5	4.0	200.0	0

a) Calculated from the yield of DMS obtained after a certain reaction time. b) Sulfilimine.

TABLE 4. EFFECT OF SUBSTITUENT



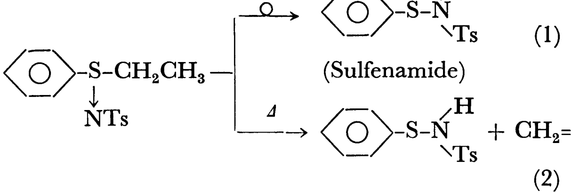
+ LiBr + DMSO;
SI^b)/LiBr = 1/4
molar ratio

X	*p*-MeO	H	*p*-NO_2	H
Y	H	H	H	*m*-NO_2
k_{rel}[a]	0.1	1.1	18.0	5.0

a) Calculated from the yield of DMS obtained after a certain reaction time. b) Sulfilimine.

was investigated. The reactivity was determined by comparing the amount of dimethyl sulfide formed after a certain reaction time. The results are summarized in Tables 3 and 4.

The ability of the triggered system (sulfilimine–lithium bromide system) toward the reduction of DMSO appears to depend considerably on the structure of the sulfilimine (Table 3), the reduction proceeding favorably in the order $PhCH_2 > i\text{-}Pr > Me > Et > Ph$. This trend of order does not seem to fit any single conceivable factor. In addition, *β*-elimination apparently takes place with the sulfilimines having *β*-hydrogen,[3] *i.e.*, Et- and *i*-Pr- derivatives, playing an important role in the catalytic reduction. The sulfenamides (1 or 2) which are formed in both reactions (rearrangement and *β*-elimination) seem to be the key compounds (Scheme 1).



Scheme 1.

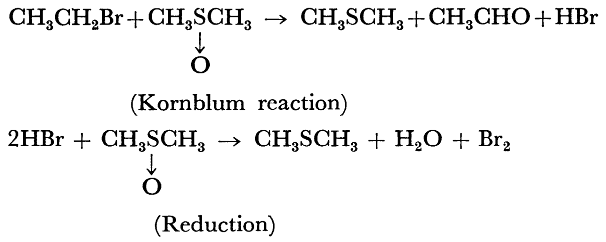
A study on the effect of substituent in the sulfilimine on this reaction reveals that the reduction is accelerated by the electron-withdrawing substituent. This trend is in line with the Stevens rearrangement reaction of the sulfilimine with halide ion.

In order to clarify the nature of the active species formed in the reaction of the SB-System and acting as a catalyst for the reduction of DMSO, the controlled experiments were carried out with various substances. The results are summarized in Table 5. All the compounds seem to have a similar triggering ability for the reduction of DMSO, and the common active species is considered to be either bromine or hydrogen bromide since both benzyl bromide and ethyl bromide generate bromine or hydrogen bromide in the reactions with DMSO, (Kornblum reaction[3]) and reduction[2])), as shown in Scheme 2.

TABLE 5. CATALYTIC REDUCTION OF DMSO

DMSO + Catalytic System; 100 : 3 (molar ratio)

Catalytic System	SB-System	$PhCH_2Br$	EtBr	Br_2	HBr
DMS-% (*vs.* DMSO)	55	55	54	56	56



$$CH_3CH_2Br + \underset{\overset{\downarrow}{O}}{CH_3SCH_3} \rightarrow CH_3SCH_3 + CH_3CHO + HBr$$

(Kornblum reaction)

$$2HBr + \underset{\overset{\downarrow}{O}}{CH_3SCH_3} \rightarrow CH_3SCH_3 + H_2O + Br_2$$

(Reduction)

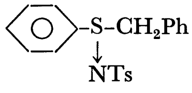
Scheme 2.

The effect of additional third components on the reduction of DMSO with the SB-System was examined. The results are given in Table 6. The active species is very likely to be molecular bromine, since the reduction was retarded remarkably when styrene was added in the reaction system, while a small amount of (1,2-dibromoethyl)benzene was detected by GLC. Although no bromo-derivative could be detected in the case of phenol, phenol is known to react readily with molecular bromine affording the corresponding *o*- or *p*-substituted derivative, thus trapping molecular bromine.

Thus, the generation of active species (bromine or hydrogen bromide) is suggested as shown in Scheme 3.

Product Analysis of the Catalytic Reduction of DMSO by Molecular Bromine. In order to simplify the catalytic system for the reduction of DMSO, molecular bromine was used as a catalyst and both the products and yields

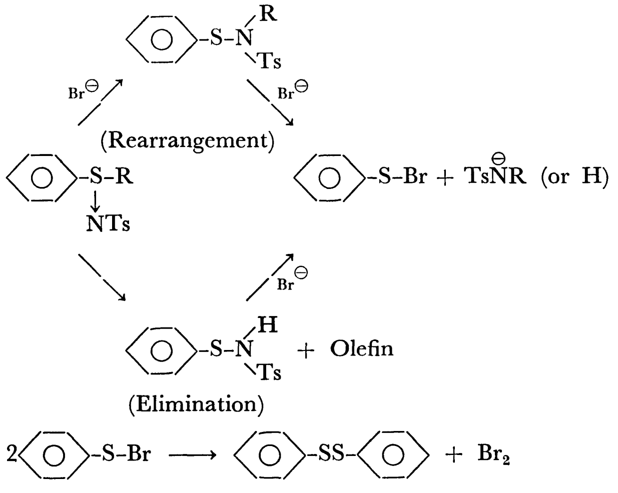
TABLE 6. EFFECT OF ADDITION OF THIRD COMPONENT



+ LiBr + Addendum; 1 : 3 : 1
(molar ratio)

Addendum	None	Styrene[a]	Cyclohexene	Phenol	Hydroquinon
DMS(%)[b]	1400	30	0	0	0

a) 1,2-Dibromoethylbenzene was detected by means of GlC. b) Conversion percentage for sulfilimine.



Scheme 3.

Table 7. Product distribution of the reduction of DMSO by bromine
($DMSO/Br_2=100/1$; molar ratio)

Products	Yields (%)	
	%-Br_2[a]	%-DMSO[b]
CH_3SCH_3	1860	56
$(CH_3)_3S^+$ $CH_3SO_3^-$	400	12
CH_3SO_3H	232	7
$(CH_2O)_n$	600	18

a) Calculated from a molar amount of Br_2. b) Conversion percentage for DMSO.

were examined. The results are given in Table 7. The reduced product is dimethyl sulfide, while the oxidized products are both methanesulfonic acid derivatives and formaldehyde, the yields of which are nearly equal.

A similar product distribution was also observed in the reduction of DMSO by a catalytic amount of hydrogen bromide or benzyl bromide (Table 4). In order to confirm the applicability of this catalytic reduction, the same experiments were carried out with various sulfoxides. The results are summarized in Table 8. Apparently the reduction depends on the structure of the sulfoxide (R or R′). Diphenyl sulfoxide is non-reactive and was recovered quantitatively even under drastic reaction conditions. This suggests that the presence of acidic hydrogen is essential. The sequence of reactivities of these sulfoxides, Me>Et>$-(CH_2)_4-$>*n*-Bu, seems to suggest that both steric and inductive effects of alkyl substituent are important in the rate determining step of the reduction.

The yield of DMS in the reduction of DMSO by bromine was followed by means of GLC (Fig. 1.). The formation of DMS increases gradually at the initial stage of the reduction, and then the increase becomes remarkably when the reduction reaches near to completion. The formation of DMS was apparently accelerated by the initial addition of DMS. This suggests that there are at least two routes for the catalytic formation of DMS whose relative rates differ and DMS itself may accelerate the reduction. Since the reduction is not affected by radical initiating reagents such as 2,2′-azobisisobutyronitrile and oxygen atmosphere, it is undoubtedly an ionic reaction.

Table 8. Catalytic reduction of various sulfoxides $R\text{-}\underset{\downarrow \atop O}{S}\text{-}R'$ by molecular bromine
($Sulfoxide/Br_2=100/1$; molar ratio)

R	R′	Reaction conditions		Yield of sulfide	
		Temp (°C)	Time (h)	%-Br_2[a]	%-Sulfoxide[b]
Me	Me	100	5	1860	56
Et	Et	100	24	2310	69
n-Bu	*n*-Bu	100	240	1450	43[c]
$-(CH_2)_4-$		100	72	1810	54
Ph	Me	100	240	200	6[c]
Ph	Ph	100	100	0	0
				(recovered quant)	

a) Calculated from a molar amount of Br_2. b) Conversion percentage for sulfoxide. c) The starting materials were recovered in 36% and 82% for di-*n*-butyl and methyl phenyl sulfoxide, respectively.

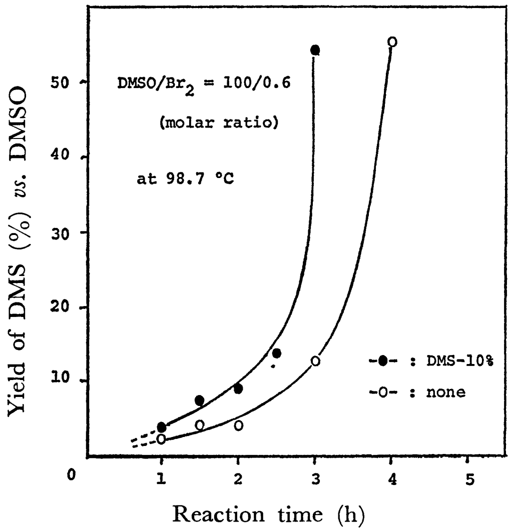


Fig. 1. The effect of DMS for the reduction of DMSO.

The effects of various salts on the reduction were also investigated (Fig. 2). Lithium chloride apparently accelerates, while both lithium bromide and lithium perchlorate retard the reduction.

These and other observations such as product analyses and the rate of formation of DMS, suggest that the reduction can be explained in terms of two main catalytic cycles (Scheme 4). The reaction is obviously initiated by the facile bromination of DMSO or DMS by bromine. The α-bromo-sulfoxide or sulfide reacts with DMSO (Kornblum reaction) affording the sulfide and oxidation products, accompanied by hydrogen bromide which is known to reduce the sulfoxide to the sulfide, forming bromine and water.[2]

If these catalytic cycles work competitively in this reaction while the cycle (2) proceeds faster than the cycle (1), an explanation can be given for the char-

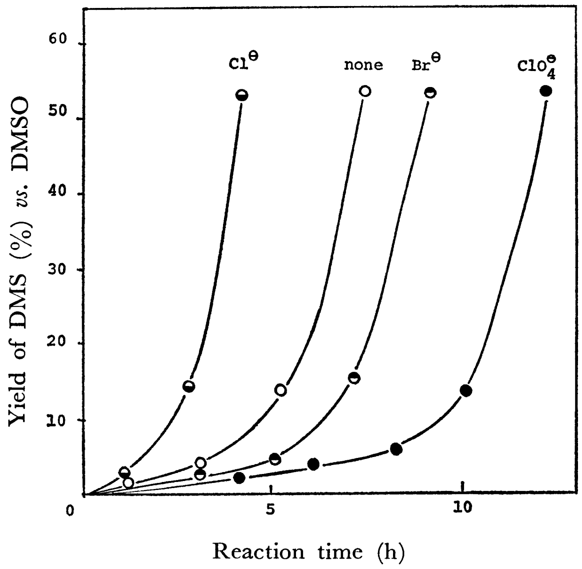
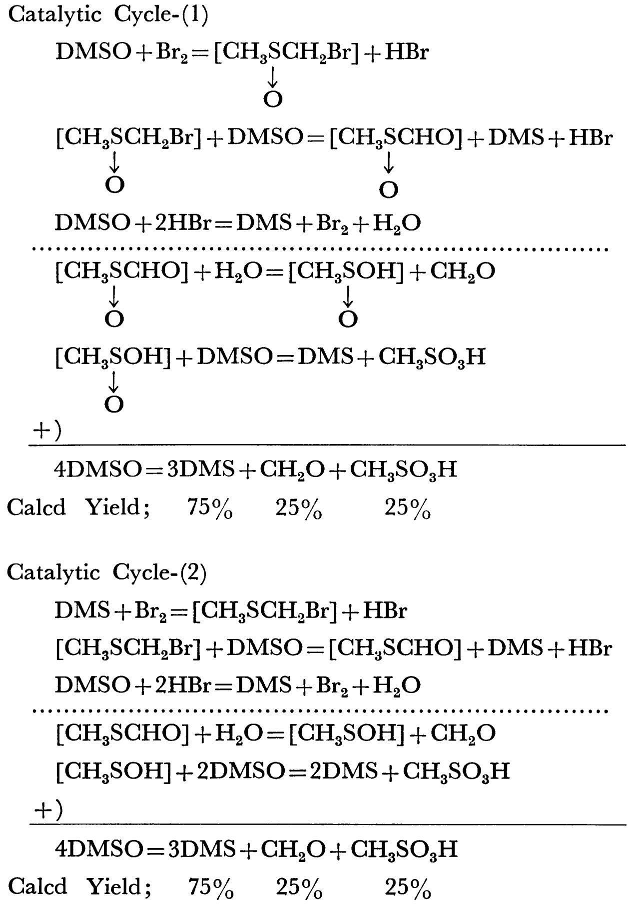


Fig. 2. Salt-effect of reduction of DMSO by bromine. $DMSO/Br_2/Salt = 100/0.35/0.35$ (molar ratio) ○ = none, ◒ = LiCl, ◓ = LiBr, ● = $LiClO_4$


Catalytic Cycle-(1)

$$DMSO + Br_2 = \underset{\overset{\downarrow}{O}}{[CH_3SCH_2Br]} + HBr$$

$$\underset{\overset{\downarrow}{O}}{[CH_3SCH_2Br]} + DMSO = \underset{\overset{\downarrow}{O}}{[CH_3SCHO]} + DMS + HBr$$

$$DMSO + 2HBr = DMS + Br_2 + H_2O$$

……………………………………………………

$$\underset{\overset{\downarrow}{O}}{[CH_3SCHO]} + H_2O = \underset{\overset{\downarrow}{O}}{[CH_3SOH]} + CH_2O$$

$$\underset{\overset{\downarrow}{O}}{[CH_3SOH]} + DMSO = DMS + CH_3SO_3H$$

+)

$$4DMSO = 3DMS + CH_2O + CH_3SO_3H$$

Calcd Yield; 75% 25% 25%

Catalytic Cycle-(2)

$$DMS + Br_2 = [CH_3SCH_2Br] + HBr$$

$$[CH_3SCH_2Br] + DMSO = [CH_3SCHO] + DMS + HBr$$

$$DMSO + 2HBr = DMS + Br_2 + H_2O$$

……………………………………………………

$$[CH_3SCHO] + H_2O = [CH_3SOH] + CH_2O$$

$$[CH_3SOH] + 2DMSO = 2DMS + CH_3SO_3H$$

+)

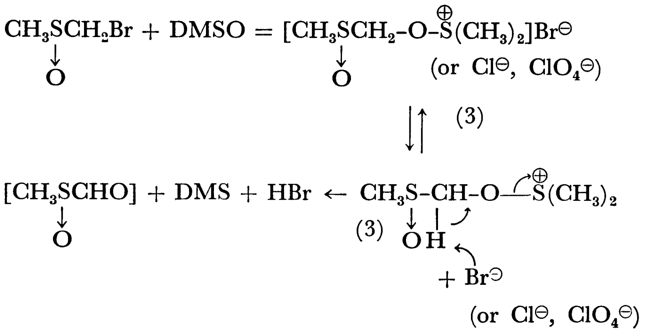
$$4DMSO = 3DMS + CH_2O + CH_3SO_3H$$

Calcd Yield; 75% 25% 25%

Scheme 4.

acteristic phenomenon of the formation of DMS, namely the gradual increase of DMS at an early stage, followed by a remarkable increase during the reaction. At the initial stage of the reaction, cycle (1) would work predominantly since the amount of DMS in the reaction mixture is too small for cycle (2) to operate; however, the accumulation of DMS during the course of reduction would gradually change the main reaction from cycle (1) to cycle (2). Since cycle (2) proceeds faster than cycle (1), the formation of DMS would increase remarkably near the completion of the reaction.

The Kornblum reaction is probably the slowest one in cycle (1), while the rate-determining step of the reaction is the proton abstraction from the oxo-sulfonium salt (3) by the counter anion (Scheme 5), in view of the interesting salt effects. Since bromide ion acts as a common salt which prevents the formation of the oxo-sulfonium salt(3), and perchlorate ion is a

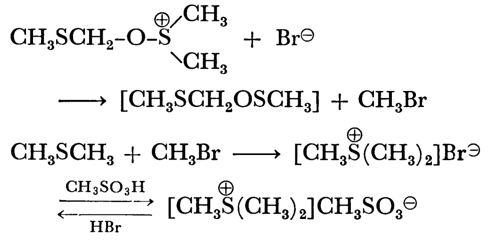


$$\underset{\overset{\downarrow}{O}}{CH_3SCH_2Br} + DMSO = [\underset{\overset{\downarrow}{O}}{CH_3SCH_2}\text{-O-}\overset{\oplus}{S}(CH_3)_2]Br^{\ominus} \quad (\text{or } Cl^{\ominus}, ClO_4^{\ominus})$$

$$\downarrow\uparrow \quad (3)$$

$$\underset{\overset{\downarrow}{O}}{[CH_3SCHO]} + DMS + HBr \leftarrow \underset{(3)}{CH_3\underset{\overset{\downarrow}{O}}{S}\text{-}\underset{\overset{|}{OH}}{CH}\text{-O-}\overset{\oplus}{S}(CH_3)_2} + Br^{\ominus} \quad (\text{or } Cl^{\ominus}, ClO_4^{\ominus})$$

Scheme 5.



$$CH_3SCH_2\text{-O-}\overset{\oplus}{S}\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix} + Br^{\ominus} \longrightarrow [CH_3SCH_2OSCH_3] + CH_3Br$$

$$CH_3SCH_3 + CH_3Br \longrightarrow [CH_3\overset{\oplus}{S}(CH_3)_2]Br^{\ominus} \underset{HBr}{\overset{CH_3SO_3H}{\rightleftarrows}} [CH_3\overset{\oplus}{S}(CH_3)_2]CH_3SO_3^{\ominus}$$

Scheme 6.

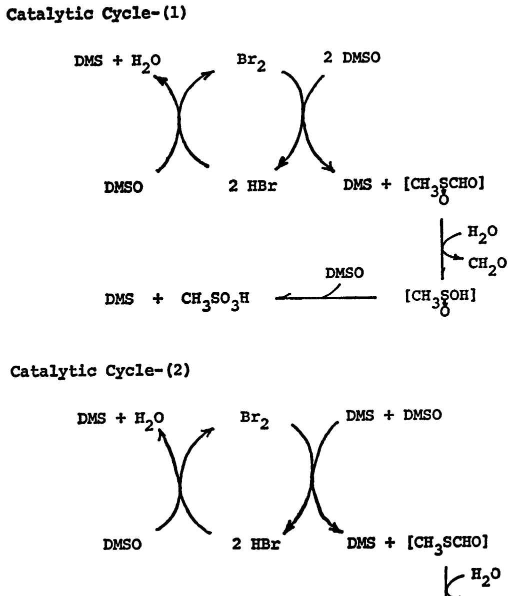


Fig. 3. Mechanism of catalytic reduction of DMSO by Br_2.

weaker base than bromide ion to abstract the proton of the oxo-sulfonium salt(3), the reduction would be retarded by perchlorate ion. Chloride ion is a stronger counter anion than bromide or perchlorate ion. Thus, the whole scheme of the catalytic reduction DMSO to DMS may be illustrated as shown in Fig. 3. The formation of trimethylsulfonium methanesulfonate ($(CH_3)_3S^+CH_3SO_3^-$) is shown in Scheme 6.

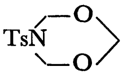
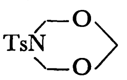
Experimental

Materials. N-p-*Tosylsulfilimine*: All the *N-p*-tosylsulfilimines were prepared from the corresponding sulfides and chloramine-T by the modified Mann-Pope reaction.[5] These sulfilimines were identified by comparison of their mp, IR, and NMR spectra with those reported.[5]

Lithium Halide and Perchlorate: Commercial anhydrous products were used without purification.

Sulfoxide: Commercial DMSO was dried over calcium hydride and distilled before use. Diethyl, tetramethylene, dibutyl, methyl phenyl and diphenyl sulfoxides were prepared by oxidation of the corresponding sulfides with bromine in acetic acid.[6]

Other Reagents: Commercial dimethyl sulfide, benzyl bromide, ethyl bromide and cyclohexene were used after distillation. Commercial styrene and phenol were distilled in order to remove the stabilizer. Commercial bromine and aqueous hydrobromic acid solution were used without purification.

Reaction of S-*Methyl* S-*Phenyl*-N-p-*Tosylsulfilimine with Halide Ion in DMSO.* A typical run is as follows; a mixture of *S*-methyl *S*-phenyl *N-p*-tosylsulfilimine (3 mmol) and lithium bromide (12 mmol) was dissolved in DMSO (5 g) containing 0.5 g of benzene as an internal standard for GLC. The solution was heated in a sealed tube at 110 °C for 12 h. The reaction mixture was then cooled to ice-water temperature. In order to determine the yield of dimethyl sulfide formed in the reaction, it was injected into the GLC-column and then poured into 30 ml of cold water. The products were extracted from the solution with chloroform and separated by column chromatography (silica gel; benzene); $TsNHCH_3$ 43%, CH_3SCH_3 1400%, $(CH_2O)_n$ 10% and  34%, respectively. The yields were calculated from the molar amount of the sulfilimine used. The structure of  was determined by the following data; IR ν_{SO_2} 1340, 1160 cm^{-1} ν_{COC} 1160 cm^{-1}; NMR is shown in Fig. 4.

Found: C, 50.2; H, 5.35; N, 5.93%. Calcd for $C_{10}H_{13}NO_4S$: C, 49.4; H, 5.35; N, 5.77%.

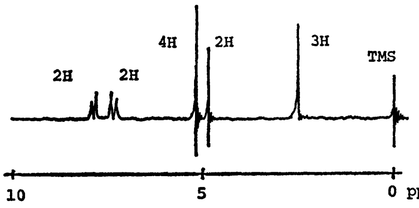
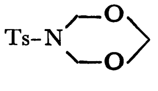


Fig. 4. NMR spectrum of  (in $CDCl_3$).

Reactions of Various N-p-*Tosylsulfilimines with Lithium Bromide in DMSO.* A mixture of the *N-p*-tosylsulfilimine (3 mmol) and lithium bromide (12 mmol) was dissolved in DMSO (5 g) containing benzene (0.5 g) as an internal standard for GLC. The solution was heated in a sealed tube at 110 °C. for 5 h, and then cooled to ice-water temperature. The isolation and determination of the products formed in the reaction were carried out as described above.

Catalytic Reduction of DMSO by Various Bromides. As a typical example, a solution of ethyl bromide (0.33 g; 3 mmol) and DMSO (8.0 g; 100 mmol) was placed into a sealed tube, and heated at 100 °C for 24 h. The yield of dimethyl sulfide was determined by GLC.

Product Analysis in the Reduction of DMSO by Bromine. The reaction was carried out by heating an ampouled mixture of bromine (1 mmol) and DMSO (8.0 g; 100 mmol) at 100 °C for 5 h. After the reaction, the reaction mixture was separated into two layers. From the upper layer dimethyl sulfide was detected by GLC as the sole product (56%). The under layer was poured into 100 ml of acetone, and then the crystalline precipitates were filtrated off and recrystallized from acetone-ethanol. The compound was identified as trimethylsulfonium methanesulfonate ($(CH_3)_3S^+CH_3SO_3^-$) by comparison of its IR and NMR spectra with those of an authentic sample prepared from trimethylsulfonium iodide ($(CH_3)_3S^+I^-$) and methanesulfonic acid. The yield of the sulfonium salt was 12%. Methanesulfonic acid was separated from the filtrate by means of the anion exchange resine (7%). Paraformaldehyde condensed in the cold part of the sealed tube (18%).

Catalytic Reductions of Various Sulfoxides by Bromine. A typical run is as follows; a mixture of bromine (0.1 mmol) and dibutyl sulfoxide (0.62 g; 10 mmol) was put into a sealed tube and heated at 100 °C for 10 days. The yield of the corresponding sulfide was determined by GLC.

Measurement of the Rate of Formation of Dimethyl Sulfide. A typical run is as follows; a mixture of bromine (0.35 mmol) and DMSO (8.0 g; 100 mmol) containing benzene (0.5 g) as an internal standard for GLC was divided into six portions which were put into separate ampoules. The ampoules were heated in a constant temperature oil bath (100 °C) at the same time, and then removed at set intervals. The yield of dimethyl sulfide was determined by GLC. The effect of the initial addition of dimethyl sulfide (5%) was observed by the same procedure as described above. Addition of various lithium salts to the reaction mixture was also carried out, the molar ratio of DMSO, bromine and lithium salt being 100 : 0.35 : 0.35.

References

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