

CATALYTIC REDUCTION OF DIMETHYL SULFOXIDE AND OTHER SULFOXIDES  
WITH BROMINE - HYDROBROMIC ACID SYSTEM.

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Recently, it was found that halide ions in DMSO or DMF catalyze rearrangement reaction of N-p-tosylsulfilimine to N-alkyl, N-thiophenoxy-p-tosyl-amide<sup>1)</sup>. However, unexpectedly, when DMSO was used as a solvent the reduction of DMSO was observed until it was consumed and the rate and the amount of reduction were varied by changing the halide ions. This reduction does not take place at all, if either sulfilimine or halide ions are absent. Therefore, the reduction of DMSO should be "triggered" by some species which will be formed as a transient intermediate arising from sulfilimine and halide ion. Furthermore, we found that most active catalysts are Br<sub>2</sub> and HBr molecule. Although the reduction of sulfoxide with other acid has been reported<sup>2)</sup>, this is the most facile and hence novel catalytic reduction of sulfoxides.

Thus, we wish to communicate this new catalytic reduction of DMSO and other sulfoxides with Br<sub>2</sub>-HBr system.

Generally the reduction was carried out by heating an ampouled mixture of 1/100 molar ratio of Br<sub>2</sub> and sulfoxide at 100°C. In the case of DMSO the products and yields obtained are summarized in Table I. The products showed revealed that the reduced product is dimethyl sulfide (DMS) and the oxidized products are both methanesulfonic acid and formaldehyde of which yields are nearly equal. Furthermore, the similar reduction of DMSO is observed with a catalytic amount of HBr. Similarly, the yields of the sulfides obtained by the

reactions of various sulfoxides with bromine are summarized in Table II.

These results reveal that the ability to reduce the sulfoxide depends on the structure of R or R'. Especially, diphenylsulfoxide was recovered almost quantitatively even under markedly drastic reaction condition suggesting that the hydrogen atom attached to  $\alpha$ -carbon atom may play an important role in this reduction.

Table I. Products and Yields of Reduction of DMSO

Products	Yields ( %-Br <sub>2</sub> ) <sup>a)</sup>	( %-DMSO ) <sup>b)</sup>
CH <sub>3</sub> SCH <sub>3</sub>	1860	56
(CH <sub>3</sub> ) <sub>3</sub> S <sup>+</sup> CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	400	12
CH <sub>3</sub> SO <sub>3</sub> H	232	7
(CH <sub>2</sub> O) <sub>n</sub>	600	18

Table II. Catalytic Reduction of various Sulfoxides ( R-SO-R' )

R	R'	Reaction Condition		Sulfide Yield	
		( °C )	( hr. )	( %-Br <sub>2</sub> )	( %-DMSO )
Me	Me	100	5	1860	56
Et	Et	100	24	2310	69
n-bu	n-bu	100	240	1450	43 ( recovd. 36 )
	-(CH <sub>2</sub> ) <sub>4</sub> -	100	72	1810	54
Ph	Me	100	240	200	6 ( recovd. 82 )
Ph	Ph	150	100	0	0 ( recovd. quant. )

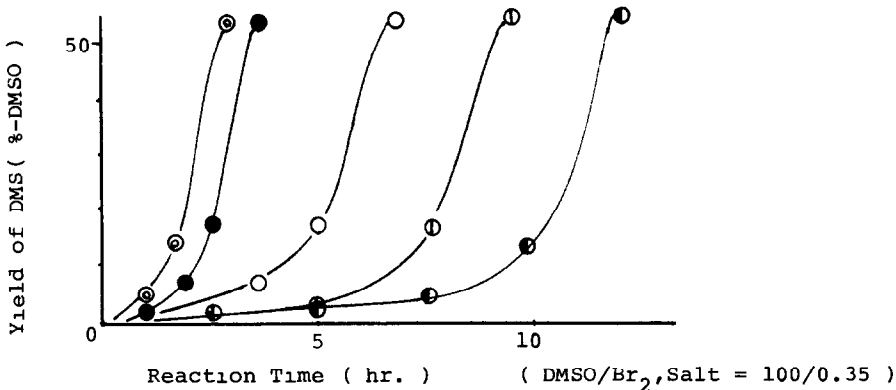
a) The conversion percentage for DMSO used.

b) The yield calculated from the mole-% based on Br<sub>2</sub>.

The amount of DMS formed in the reaction was followed by means of gas-chromatography. Together with the various salt effects on the reaction the results obtained are illustrated in Fig. I.

From these results shown in Fig. I the following characteristic features can be deduced ; (1) the formation of DMS is observed gradually and then increased remarkably as the reaction proceed near to the completion, (2) the reaction was also accelerated by the addition of DMS, (3) the reaction was considerably affected by the addition of various salts, namely, lithium chloride accelerated however both lithium bromide and perchlorate retarded the reaction.

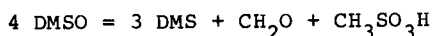
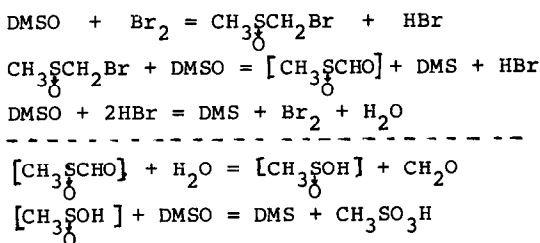
Therefore, the product analysis and characteristic features for the rate of



○ = non., ⊙ = LiCl, ⊕ = LiBr, ⊖ = LiClO<sub>4</sub>, ● = initial addition of 5%-DMS  
 Fig. I. Rate of formation of dimethyl sulfide.

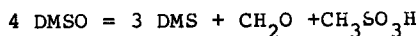
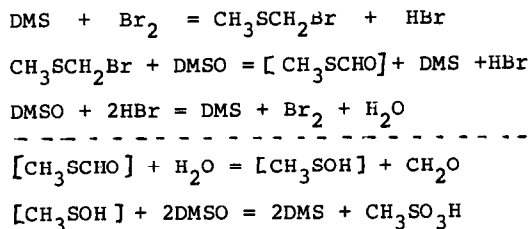
formation of DMS can be explained in terms of two catalytic cycles. If these cycles compete mutually in this reaction and the cycle-II proceeds preferentially and faster than the cycle-I, the characteristic phenomenon of the formation of DMS can be nicely explained.

Catalytic Cycle-I



( theoretical yields of DMS = 75 %, CH<sub>2</sub>O = 25%, CH<sub>3</sub>SO<sub>3</sub>H = 25% )

Catalytic Cycle-II



Obviously, the reaction is initiated by the facile bromination of DMSO by Br<sub>2</sub>. Then the α-bromosulfoxide reacts with DMSO ( Kornblum Reaction<sup>3</sup>) to give the sulfide and oxidation product generating HBr which is known to reduce the sulfoxide to the sulfide. If we postulate that the Kornblum reaction( shown in scheme - I ) is the slowest step, the salt effects can be explained as follows ; bromide ion acts as a common salt which prevents the dissociation of the oxy-

sulfonium salt, perchlorate ion is working as a weaker base than bromide ion to abstract the proton of the sulfonium salt, meanwhile, chloride ion is a stronger counter anion of the salt facilitating the sulfide formation. The whole scheme of the catalytic reduction of DMSO to DMS is illustrated in Fig. II.

Further studies on the detailed mechanism and the application of this novel reductive method are now underway.

Scheme - I. " Kornblum Reaction "

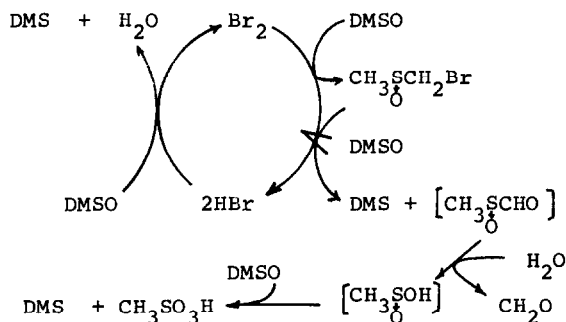
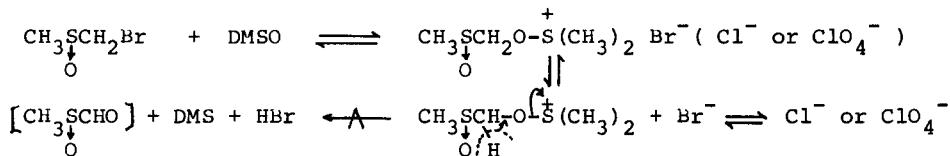


Fig. II. Mechanism of Catalytic Reduction of DMSO

References

- 1) N. Furukawa, T. Aida and S. Oae, *Int. J. Sulfur Chem.*, A-2, 181(1972).
- 2) T.L. Fletcher, H.L. Pan, *J. Org. Chem.*, 24, 141(1959).  
E.N. Karaulova, G.D. Galpern, *Zhur. Obshech. Khim.*, 29, 3033(1959).
- 3) N. Kornblum, W.J. Jones, G.J. Anderson, *J. Amer. Chem. Soc.*, 81, 4113(1959)