

OXYGEN EXCHANGE REACTION OF SULFOXIDES WITH DIMETHYL SULFOXIDE (1)

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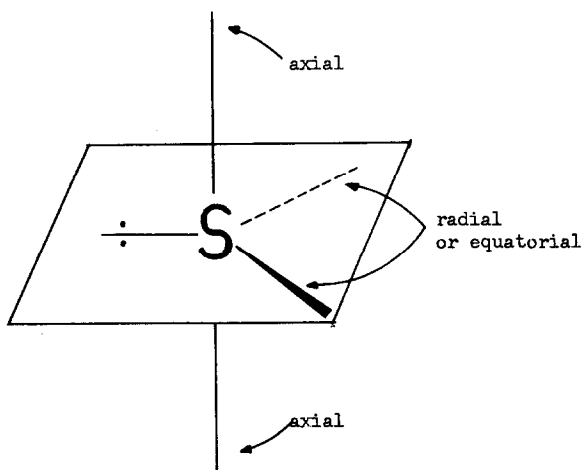
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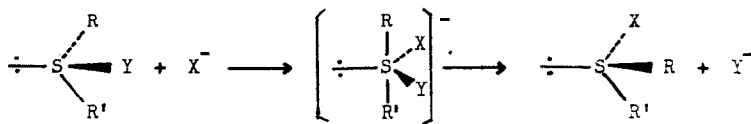
When an intermediate or an incipient activated complex at the transition state of a nucleophilic substitution reaction on the trivalent sulfur atom is considered to be a trigonal bipyramidal structure, two possible stereochemical consequences will arise depending upon the steric arrangement of both incoming and outgoing groups.

When both the entering and leaving groups are assumed to occupy the axial positions, the process is similar or identical to SN-2 reaction on carbon atom and the net result is expected to be the inversion of configuration.

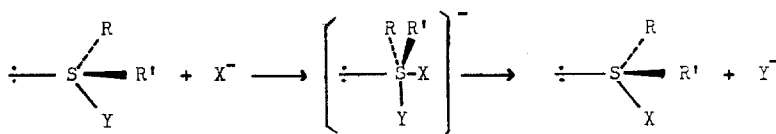
Fig. I



A similar net inversion will be resulted also when both incoming and outgoing groups assume radial position as shown below.



A possible example may be the recent work of Day and Cram who showed that the formation of sulfilimine from the corresponding sulfoxide resulted in net inversion (2). Another example may be the oxygen exchange reaction of sulfoxides with epoxy compound which will be published in a separate communication. If both incoming and outgoing groups assumes axial and radial positions, namely the perpendicular arrangement, the reaction will lead to the retention of configuration.

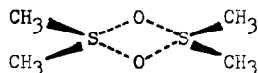


In this communication we wish to report the first example of this type of reaction of sulfoxides, namely the oxygen exchange reaction with dimethyl sulfoxide, which leads to the product retaining the original configuration.

The oxygen exchange reaction is quite useful for the study on nucleophilic reactions on the trivalent sulfur atom because one can readily prepare both ^{18}O -labeled (3) and optical active (4) sulfoxides while the analysis of ^{18}O -content in sulfoxides is also quite facile.

Meanwhile, dimethyl sulfoxide is suggested to be associated as shown below (5).

Other sulfoxides are also considered to be associated similarly (6).



Therefore, if oxygen interchange takes place among sulfoxides there is a possibility that the oxygen exchange proceeds through the bimolecular internucleophilic attack within the associated bimolecular structure. Then one can expect that the oxygen exchange will result in the net retention.

We have examined the possible oxygen exchange between *p*-tolyl methyl sulfoxide with dimethyl

sulfoxide. The results are shown in Table I.

As we have anticipated, the oxygen exchange took place substantially when heated around 150°C for 24 hrs under which the racemization was very little.

The reaction apparently involves the participation of the 3d-orbitals of the central sulfur atom forming a sp^3d configuration whereby the entering and the leaving oxygen atoms lie perpendicular to each other as shown in Fig. I.

TABLE I.

Kinetic Data on Oxygen Exchange Reaction of p-Tolyl Methyl Sulfoxide with Dimethyl Sulfoxide

^{18}O -Exchange Reaction* at 150°C

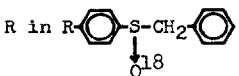
No.	^{18}O -Content	Time (hrs.)	No.	^{18}O -Content	Time (hrs.)
1	1.288	0	1	+144.2	0
2	1.015	8	2	143.7	9
3	0.769	16	3	143.1	18.15
4	0.507	24	4	143.3	26
			5	143.2	35
			6	142.6	45
			7	142.9	57

* p-Tolylmethyl sulfoxide; 10^{-2} mole was reacted
with 25 ml of DMSO $k_{\text{ex.}} = 1.21 \times 10^{-5}(\text{sec}^{-1})$
 $k_{\text{ex.}}/k_{\text{rac.}} \gg 1$

It is interesting to note that the oxygen exchange is more facile with p-tolylmethyl sulfoxide than with chlorophenyl methyl sulfoxide ($k = 3.22 \times 10^{-6} \text{ sec}^{-1}$ at 150°). Perhaps the S-O bond cleavage is more facile with the former compound because of the electron-releasing nature of methyl group. A similar results were obtained in the reaction of aryl benzyl sulfoxide with dimethyl sulfoxide. (Table II)

TABLE II

Oxygen Exchange Reaction of Aryl Benzyl Sulfoxide with Dimethyl Sulfoxide at 150° for 10 hrs^{a)}

R in R- 	¹⁸ O-concentration of starting sulfoxide (atom %)	% ¹⁸ O exchange
CH ₃	1.08	36
H	1.06	0
NO ₂	1.15	0

a) Sulfoxide, 5×10^{-3} mole, was reacted with 25 ml of Dimethyl sulfoxide.

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