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Conformation and S=O Stretching Absorptions of Simple Sulfoxides

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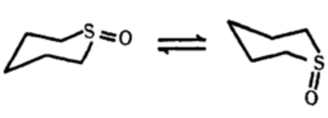
The infrared S=O stretching absorptions of several simple sulfoxides have been measured. Some sulfoxides show one absorption maximum, whereas others show two. These results may be attributed to the rotational isomerism about the S–C axis. Convincing evidence for this conclusion has been obtained by the measurement of the spectra of methyl isopropyl sulfoxide at various temperatures.

The conformation of thian oxide has been discussed on the basis of various pieces of evidence. An X-ray diffraction study of *trans*-1,4-dithian 1,4-dioxide has led to the conclusion that the S=O axial conformation is present in the crystals.[1] The nuclear magnetic resonance spectrum of the same compound also supports the idea that the stable conformation is the S=O axial form.[2] On the other hand, it has been claimed from the thermal equilibration of thian 1-oxide that the stable form of the compound is the S=O axial chair (2).[3] Since the axially-substituted isomer of cyclohexane is well known to be less stable than the equatorial, there must be some force operating to stabilize the axial form of the thian oxide or to destabilize the equatorial form.[1] Their stereochemical interest in the thian oxide derivatives has led the present authors to examine the infrared spectra of several simple sulfoxides.



(1) (2)

During the course of this study, Cairns *et al.* reported that the multiplicity of the S=O stretching absorption of sulfoxides could be explained by the Fermi resonance.[4] The data accumulated in this laboratory agree with those obtained by Cairns and his co-workers in the sense that sulfoxides sometimes give multiple absorption bands in the region of 1100—1000 cm^{-1}, but not on the origin of this phenomenon. The purpose of this communication is to present the basis upon which the authors would like to ascribe the phenomenon to

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[1] H. M. M. Shearer, *J. Chem. Soc.*, **1959**, 1394.

[2] C.-Y. Chen and R. J. W. LeFevre, *Austr. J. Chem.*, **16**, 917 (1963).

[3] C. R. Johnson and D. McCants, Jr., *J. Am. Chem. Soc.*, **86**, 2935 (1964); *ibid.*, **87**, 1109 (1965).

[4] T. Cairns, G. Eglinton and D. T. Gibson, *Spectrochim. Acta*, **20**, 31 (1964).

the presence of the rotamers about the C–S bonds.

Experimental

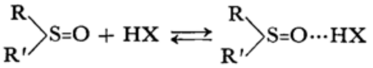
The infrared spectra were measured on a Perkin-Elmer 112 G grating spectrophotometer (slit width: 1.6 cm^{-1}) and a Japan Optics Co., Ltd., 402 G spectrometer. In every case the agreement of the data of the two instruments was good. The samples were dissolved in carbon disulfide or carbon tetrachloride to make up *ca.* 0.05 mol/*l* solution unless otherwise mentioned. The temperature dependence of the spectra was determined using liquid cells consisting of a Hg-Sn amalgam spacer and KBr discs at 0.03 mol/*l* concentration in carbon disulfide.

The spectra were scanned in the region of 1100—1000 cm^{-1} and were compared with those of the parent sulfide in order to eliminate absorptions due to skeletal vibrations. This technique, together with the operation to form an intermolecular hydrogen bond, removed the difficulty in assigning the S=O stretching absorption band.

Materials were prepared and purified according to the literature, and the physical constants were measured in order to check the purity. Special care was taken to avoid moisture during the handling of the lower homologs.

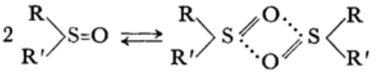
Results and Discussion

Some of the sulfoxides show single absorption bands and others, doublet absorption bands. In order to clarify the origin of these bands, two techniques were used. One was the comparison of the spectra measured in carbon tetrachloride or carbon disulfide with those obtained in chloroform. The other was the comparison of the spectra of the sulfoxide obtained in carbon tetrachloride with those obtained by adding phenol to carbon tetrachloride. In every case, the bands observed in a carbon tetrachloride solution diminish in intensity when measured in chloroform or when phenol is added, and new bands are observed at *ca.* 1020 cm^{-1} and at a frequency lower than the original by *ca.* 20 cm^{-1}. Although it was not possible to erase completely the bands at 1070—1040 cm^{-1} by these techniques, the results mentioned above are good evidence that there is an equilibrium, such as is shown by Eq. (1), because the reduced intensity corresponds to the decreased population of the free sulfoxide and the new band at a lower frequency is an indication of the formation of the hydrogen bond. Thus, one or two bands of sulfoxide in the 1070—1040 cm^{-1} region can be assigned to S=O stretching vibrations. These facts, together with the findings that some symmetrical sulfoxides have only one absorption, whereas the unsymmetrical sulfoxides usually have two, are not in agreement with the postulation by Cairns *et al.*[4]



$$\begin{matrix}R\\R'\end{matrix}\!\!>\!S{=}O + HX \rightleftarrows \begin{matrix}R\\R'\end{matrix}\!\!>\!S{=}O\cdots HX \qquad (1)$$

Other possible causes for the appearance of multiple absorptions for the S=O stretching vibration are: 1) solute-solvent interactions, 2) solute-solute interactions, 3) the coupling of vibrations, and 4) equilibrium among rotational isomers. The possibility of 1) can be disregarded because multiple absorption is observed even in carbon tetrachloride and carbon disulfide solutions, in which no significant solute-solvent interactions are to be expected. There is a possibility that monomer-dimer equilibrium (Eq. (2)) is a cause of the doublet nature of the bands, but the dependency of the absorption upon the concentration of the solute (to be discussed below), together with the fact that this possibility cannot be the reason why some sulfoxides give one band while others give two, are good indications that it is not really the case.



$$2\ \begin{matrix}R\\R'\end{matrix}\!\!>\!S{=}O \rightleftarrows \begin{matrix}R\\R'\end{matrix}\!\!>\!S\begin{matrix}\diagup\!\!\!\!\diagup O\cdots\\ \cdots O\diagup\!\!\!\!\diagup\end{matrix}S\!<\!\begin{matrix}R\\R'\end{matrix} \qquad (2)$$

The S=O stretching absorptions of dimethyl sulfoxide and methyl isopropyl sulfoxide in carbon disulfide were measured in solutions from 3 to 0.0003 mol/*l*. The results indicate that when the concentration is higher than *ca.* 0.5 mol/*l* the shape of the spectra changes, but it does not in solutions of less than 0.1 mol/*l* concentration. Thus, Beer's law is applicable to the absorption when the concentration is less than 0.1 mol/*l*.[*1]

With the above discussions in mind, it seems attractive to consider that the origin of the multiplicity of the S=O stretching bands is the rotational isomerism. Two C–S bonds must be considered when one discusses the isomerism of sulfoxides. Projection through one of the C–S axes may be given as I—III.[*2] I is the conformation in which S=O oxygen staggers between two hydrogens.

[*1] The authors prefer, in this connection, to say that the association of sulfoxide occurs according to Eq. (2) when the concentration is higher than 0.5 mol/*l*. This opinion conflicts with the report[5] by Mislow *et al.* that a sulfoxide forms a dimer in the concentration range of 0.02—0.06 mol/*l*, but it is almost unbelievable that the dimer survives even at the concentration of 0.0003 mol/*l*, where no change of spectra was observed. The matter is still to be explored. However, the following discussions are not affected whether the sulfoxide is a monomer or a dimer unless significant populations of monomers and dimers are present due to equilibration.

5) K. Mislow, M. G. Green, P. Laur and D. R. Chisholm, *J. Am. Chem. Soc.*, **87**, 665 (1965); see also R. F. Watson and J. F. Eastham, *ibid.*, **87**, 664 (1965).

[*2] The present authors adopt this classification mainly because of the success of similar classification in alcohols; primary, secondary, and tertiary alcohols were shown to possess O–H stretching absorptions according to their classes.[6]

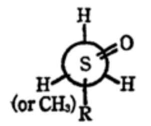
6) M. Ōki and H. Iwamura, This Bulletin **32**, 950 (1959).

TABLE 1. ABSORPTION OF DIALKYL SULFOXIDES DUE TO S=O STRETCHING (*ca.* 0.1 mol/*l* solution in carbon tetrachloride) (RSOR′)

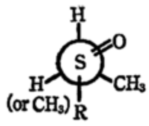
R	R′	Conformations	ν_{max} (cm^{-1})	$\varepsilon^{a)}$
CH_3	CH_3	I+I	1069	385
CH_3	C_2H_5	I+I, I+II	1065	186
CH_3	$(CH_3)_2CH$	I+II, I+III	1065 1054	268 245
CH_3	$(CH_3)_3C$	I+III	1058	356
C_2H_5	C_2H_5	I+I, I+II, II+II	1065 1058	250 (210)
C_2H_5	$(CH_3)_2CH$	I+II, I+III, II+II, I+III	1065 1056	178 245
C_2H_5	$(CH_3)_3C$	I+III, II+III	1056 1045	315 244
$(CH_3)_2CH$	$(CH_3)_2CH$	II+II, II+III, III+III	1058	312
$(CH_3)_2CH$	$(CH_3)_3C$	II+III, III+III	1050 1040	300 (160)
$(CH_3)_3C$	$(CH_3)_3C$	III+III	1040	412

a) The numbers in parentheses involve considerable uncertainty because these bands are observed as shoulders.

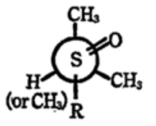
Similarly, S=O oxygen staggers between methyl and hydrogen and between two methyls in the II and III conformations respectively.



(I)



(II)



(III)

Looking at the results listed in Table 1, it is rather striking that the data fit in well with the idea of rotational isomerism. Thus, dimethyl sulfoxide can assume only one conformation (a combination of I and I; *i. e.*, Newman projections written through two C–S axes can be presented by I) whatever potential minima are taken, as long as the ethane-like potentials are postulated; indeed, it has only one absorption. Likewise, di-*t*-butyl sulfoxide (a combination of III and III) and methyl *t*-butyl sulfoxide (a combination of I and III) can take only one stable conformation and give only one absorption band. Column 3 of Table 1 lists all the possible conformations of sulfoxides. It is noticeable that some are able to take more conformations than the number of absorption bands, but no compound has more absorption bands than the number of conformations possible for the sulfoxides. The exact reason for the apparent lack of conformity between the number of conformations and that of absorptions is not known, but, it may be attributed to the scarce population of certain rotamers due to steric and/or thermodynamical reasons or to the poor resolution of the instrument.

It is tempting, from the data, to postulate that a conformation gives rise to a characteristic absorption in a certain range; the classification may be summarized as is shown in Table 2. The reason for the effect of alkyl branching (the shift to a lower frequency) is not quite understood at present, but it may be either the inductive effect of the alkyl group and/or a possible interaction between C–H and S=O groups, as will be discussed later.

TABLE 2. CORRELATION BETWEEN THE CONFORMATIONS OF SULFOXIDE AND S=O STRETCHING ABSORPTIONS

Conformation (combination of)	$\nu_{S=O}$ (cm^{-1})
I and I	1069
I and II	1065
I and III II and II	1058—1054
II and III	1051—1045
III and III	1040

Simpler examples are alkyl aryl sulfoxides, whose S=O stretching absorption data and their conformations are given in Table 3. In these cases the rotation about the C_{Ar}–S bond can be neglected, because a single conformation is so favored that its contribution is overwhelming as long as the phenyl ring is substituted symmetrically.*3

It will be noted that *p*-tolyl methyl sulfoxide gives only one band because only one conformation is possible. The same reason can be given for the

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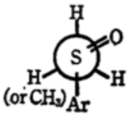
*3 In this respect, it is interesting to note that *o*-tolyl methyl sulfoxide gives three bands in the S=O stretching region, 1073, 1060 and 1040 cm^{-1}, all of which are diminished in intensity when dissolved in chloroform; after a dissolution, also, a new band is observed at 1032 cm^{-1}.

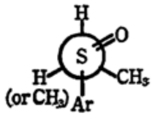
TABLE 3. S=O STRETCHING ABSORPTION DATA OF ALKYL ARYL SULFOXIDES IN CARBON DISULFIDE (ArSOR)

Ar	R	Conformations*			$\nu_{S=O}$ (cm^{-1})
p-$CH_3C_6H_4$	CH_3	IV			1062
C_6H_5	C_2H_5	IV	V		1056, 1048
C_6H_5	$(CH_3)_2CH$		V	VI	1052, 1047
C_6H_5	$(CH_3)_3C$			VI	1048

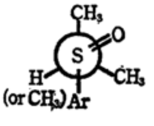
* Conformations may be represented as follows.



(IV)



(V)



(VI)

presence of one band in phenyl t-butyl sulfoxide. Phenyl isopropyl sulfoxide and phenyl ethyl sulfoxide can have two stable conformations and possess two S=O stretching absorptions. Thus, it may be said that the IV conformation gives rise to a band at 1065—1055 cm^{-1}. Similarly, the V and VI conformations give bands at 1055—1050 and 1048 cm^{-1} respectively.

The possibility of a coupling of vibrations can not be ruled out completely because the lower frequency region has not been extensively studied, but the possibility of rotational isomerism is so great, as has been discussed above, that the coupling is less likely.

The most convincing evidence for the idea that the multiplicity of the S=O stretching absorptions is attributable to the rotational isomerism is obtained by measuring the spectra at various temperatures. Methyl isopropyl sulfoxide was selected as an example to study the temperature dependence of the spectra because this compound shows a distinctly two-peaked band and possesses only two possible classes of rotational isomers. The results are shown in Fig. 1.

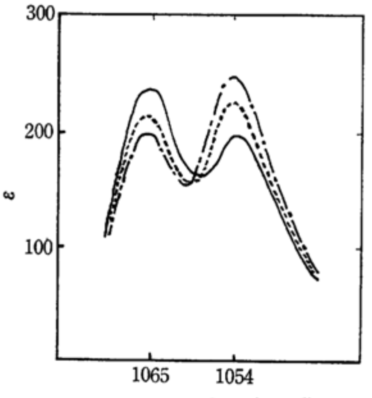
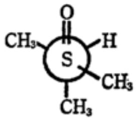


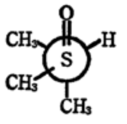
Fig. 1. Temperature dependence of S=O stretching absorptions of methyl isopropyl sulfoxide: room temperature (——), −10—−20°C (······), and −50—−80°C (—·—).

It is apparent that the intensity at the lower frequency increases at the expense of the other band when the temperature is lowered, the results lending firm support to the idea of rotational isomerism.

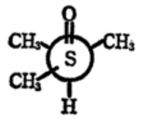
It is not thermodynamically possible for a stable isomer to be less populated at any temperature. Therefore, if it is assumed that the absorption intensity per molecule is the same for any kind of rotamer, the observed change in intensity seems to contradict the thermodynamical considerations. The apparent contradiction can, however, be overcome when the statistical factor is considered; namely, there are two conformations (VII and VIII) which give rise to the absorption at a higher frequency, whereas there is only one conformation which corresponds to the absorption at a lower frequency (IX).[*4]



(VII)



(VIII)



(IX)

These considerations inevitably lead to the conclusion that the IX conformation is more stable than VII and VIII. No convincing evidence accounting for the stability of IX has yet been obtained, but two items are worthy of note. The first is the assumption that the steric bulkiness of the oxygen atom in sulfoxide is less than that of the lone-pair electrons, and the second is the possibility of the existence of a hydrogen bond between the methyl group and the oxygen atom of sulfoxide. The first possibility arises in connection with the fact that the S=O axial form is more stable than the equatorial in thian 1-oxide, but the same reasoning may also be used in favor of the second possibility. Work is now in progress attempting to distinguish these possibilities.

[*4] The mirror images of rotamers, VII, VIII, and IX, are neglected in these discussions, because each enantiomer should exist in an equal quantity.