

SULFOXIDES AS LIGANDS. II. THE INFRARED SPECTRA OF SOME DIMETHYL SULFOXIDE COMPLEXES

BY F. A. COTTON, R. FRANCIS AND W. D. HORROCKS, JR.

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

Received April 29, 1960

The infrared spectra of dimethyl sulfoxide, dimethyl sulfoxide- d_6 , $[(CH_3)_2SO]I$, $[(CH_3)_2SO]NO_3$, $[(CD_3)_2SO]I$, $[(CH_3)_2SOCH_2]NO_3$ numerous complexes of dimethyl sulfoxide with metal salts and a few complexes of dimethyl sulfoxide- d_6 with metal salts are reported and discussed. Assignments are proposed for the bands observed in the region 650–4000 cm^{-1} . The effects of complex formation and sulfoxonium ion formation by dimethyl sulfoxide upon its S–O stretching frequency are given particular attention and it is shown that the observed shifts may be correlated with the occurrence of S– or O–bonding in the adducts by considering the electronic nature of the S–O linkage.

Introduction

We have prepared a large number of compounds containing dimethyl sulfoxide (DMSO) as a ligand.¹ In many cases the structures of the compounds have been inferred from magnetic data and electronic spectra. Realizing at the outset that the infrared spectra could also be of value in deducing the structures of many of the compounds, a thorough vibrational study of $(CH_3)_2SO$ and $(CD_3)_2SO^2$ along with the thionyl halides³ was undertaken in order that we might have at our disposal the most definite possible knowledge of the assignments for DMSO before attempting to assign the observed spectra of the complexes containing DMSO. Our analysis of the DMSO spectrum is now virtually complete and will be published separately. In this paper we shall use the information obtained from that study to analyze the spectra of a representative group of the DMSO complexes we have prepared.

Results and Discussion

The results of the thorough study of DMSO and DMSO- d_6 are the basis for analyzing the spectra of the complexes, and therefore they must be summarized first. The observed infrared bands are listed in Table I, together with assignments based upon our analysis of the entire body of infrared and Raman data which will be published separately.

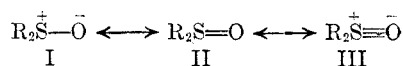
In considering the spectra of the complexes, our chief interest will be in the behavior of the SO stretching frequency, since this should be most informative with respect to the nature of the metal–ligand bonding. The reason for this follows from the bond structure of the sulfoxide group. A considerable body of data on bond lengths and dipole moments of sulfoxides leads to the conclusion that the SO bond has an order around two.^{4–8} This can be considered to be the result of resonance between the structures

TABLE I

INFRARED SPECTRA OF $(CH_3)_2SO$ AND $(CD_3)_2SO$ IN THE 600–4000 CM^{-1} REGION

$(CH_3)_2SO$		$(CD_3)_2SO$		Assignments ^c
Solu- tion ^b	Vapor	Solu- tion ^b	Vapor	
3000m	2973m	2250m	2250m	Asym. C–H str.
2918m	2908m	2133w	2133w	Sym. C–H str.
....	2183w	2185w	2 × (S–O str)
....	1455m
1436s	1440ms ^d	1084s,sh	Asym. $CH_3(CD_3)$ Def.
1416m	1419m ^d	1043m	
1404m	1405m	Sym. $CH_3(CD_3)$ Def.
1325w,sh	1319w,sh	1034s	1025m	
1306m	1304m	1005m	1015m	
1291w,sh	1287m	
....	1111s,sh	1109s,sh	S–O str.
1055vs,bd	1102vs	1064vs	1096vs	
....	1094s,sh	$CH_3(CD_3)$ rocks
1012s	1016m	824m,sh	
....	1006m	811m	815m	
946s	829w	803m,sh	
921m	915w	756m,sh	Asym. C–S str.
887w	898w	748m	750m	
690s	689m ^e	619	Sym. C–S str.
661m	672m ^e	611	

^a s = strong; m = medium; w = weak; v = very; sh = shoulder; bd = broad. ^b Chloroform and carbon disulfide solvents. ^c str = stretch; def. = deformation; sym. = symmetric; asym. = asymmetric. ^d Obscured by the strong broad S–O stretching band at 1064 cm^{-1} . ^e The spectrum of $(CD_3)_2SO$ in solution was not recorded below 650 cm^{-1} .



with II probably dominant. Similar considerations apply to the PO bond in phosphine oxides.⁸ On this premise, it would be expected that coordination of the oxygen atom in R_2SO or R_3PO would result in a lowering of the SO and PO bond orders by decreasing the contributions of II and III. This will then operate to lower SO and PO stretching frequencies. It must also be noted, however, that coordination will also tend to raise the SO and PO stretching frequencies because of the usual kinematic effect of coupling two oscillators.⁸ Experimental results on phosphine oxide complexes^{8,9} have shown, however, that the bond order lowering dominates so that the net effect is a lowering of PO stretching frequencies by ~50 cm^{-1} in phosphine oxide complexes. We therefore expect to find a similar effect in sulfoxide complexes.

With sulfoxides, however, there exists a pos-

(1) F. A. Cotton and R. Francis, *J. Am. Chem. Soc.*, **82**, 2986 (1960).

(2) F. A. Cotton, J. H. Fassnacht, W. D. Horrocks, Jr., and N. A. Nelson, *J. Chem. Soc.*, 4138 (1959).

(3) F. A. Cotton and W. D. Horrocks, Jr., *Spectrochem.* **16**, 358 (1960).

(4) C. W. N. Crumpler and S. Walker, *Trans. Faraday Soc.*, **52**, 193 (1956).

(5) M. Lister and L. E. Sutton, *ibid.*, **35**, 497 (1939).

(6) S. C. Abrahams, *Acta Cryst.*, **10**, 417 (1957).

(7) P. W. Allen and L. E. Sutton, *ibid.*, **3**, 46 (1950).

(8) F. A. Cotton, R. D. Barnes and E. Bannister, *J. Chem. Soc.*, 2199 (1960).

(9) J. C. Sheldon and S. Y. Tyree, *J. Am. Chem. Soc.*, **80**, 4775 (1958).

sibility which has no parallel with phosphine oxides. It is possible for a sulfoxide to coordinate *via* the sulfur atom, which has a lone pair. In this case, the contribution of structures II and III will be enhanced and the bond order raised. Again, there will be the kinematic effect tending to raise the SO frequency, so that we may confidently expect the overall effect of coordination of a sulfoxide *via* sulfur to be a marked exaltation of the SO stretching frequency.

Before applying these principles to the analysis of the spectra of complexes of DMSO with metal ions and Lewis acids, we may demonstrate their validity by considering the infrared spectra of some S-alkyl and O-alkyl sulfoxonium salts.^{10,11} An S-alkyl sulfoxonium salt was first reported by Kuhn and Trischman, but it was Smith and Winstein who showed that the metastable O-alkyl isomers usually exist, and they isolated a number of representative S-alkyl and O-alkyl sulfoxonium salts of DMSO.

As a typical S-alkyl salt we have chosen $[(\text{CH}_3)_3\text{SO}]^+\text{I}^-$. Its infrared spectrum was reported by Kuhn and Trischman,¹⁰ but in order to be quite certain of correctly identifying the SO stretch we have also recorded the spectrum of $[(\text{CH}_3)_3\text{SO}]^+\text{I}^-$. The results are presented in Table II. There can be no doubt that the SO stretch is at 1233 cm^{-1} , which represents a frequency increase of $\sim 135 \text{ cm}^{-1}$ over the figure for gaseous DMSO, and $\sim 178 \text{ cm}^{-1}$ over that for the solution, in agreement with the theory advanced above. Similarly $[(\text{CH}_3)_3\text{SO}]\text{NO}_3$ has a very strong, sharp absorption band at 1210 cm^{-1} assignable to SO stretching.

TABLE II

Compound ^a		Assignments
$[(\text{CH}_3)_3\text{SO}]\text{I}$	$[(\text{CD}_3)_3\text{SO}]\text{I}$	
2965s	2240s	Asym. C-H(C-D) stretches
2892m	2120m	Sym. C-H(C-D) stretches
1418ms	1215m	Asym. $\text{CH}_3(\text{CD}_3)$ deformations
1408s	1192m	
1377w	1021m	Sym. $\text{CH}_3(\text{CD}_3)$ deformations
1341w	1006vw,sh	
1315m		
1233vs	1240vs	
1222m,sh	858s	CH_3 rocks
1039vs	840w,sh	
954s	764w	
757m		S-C stretch

^a s = strong; m = medium; w = weak; v = very; sh = shoulder.

The O-methyl sulfoxonium salt studied was the nitrate since the O-methyl iodide is not known and more easily synthesized tosylates and brosylates described by Smith and Winstein¹¹ contain sulfonate groups which would confuse the spectral region of interest. The infrared spectrum of the O-methyl sulfoxonium nitrate has no bands between 1075 and 1300 cm^{-1} . There are several broad bands in the 1050–925 cm^{-1} region among which must be the SO stretch, in agreement with expectation of

a downward shift. Because of the difficulties attending the synthesis and handling of this compound, no effort was made to prepare a deuterated analog.

We now turn to the assignment of the spectra of the complexes. The spectra are all in general fairly similar, there being no pronounced dependence upon the number of coordinated molecules of DMSO or on the particular metal atom. Of course, compounds containing complex anions such as nitrate and perchlorate show bands characteristic of these species; these bands will not be considered in the following discussions. We shall show, however, that there are certain features of the spectra which can be used to infer that in most complexes the sulfoxide is attached through the oxygen atom, while in a few others, it is bound through sulfur.

We discuss the O-bonded complexes first. In Table III the complete spectra of two chemically rather different but representative compounds of this class are given, including in each case data for the analogous DMSO- d_6 compounds. From these data, it can be seen that the SO stretching band has moved down to 950 cm^{-1} in the $[\text{Co}(\text{DMSO})_6]^{+2}$ ion and even further, to 915 cm^{-1} , in $\text{SnCl}_4 \cdot 2\text{DMSO}$. In the undeuterated $[\text{Co}(\text{DMSO})_6]^{+2}$ there are strong bands both at ~ 1000 and at $\sim 950 \text{ cm}^{-1}$, and, without the data for the deuterated analog, there would be no way to be certain which of these bands should be assigned to SO stretching. The other assignments in Table III follow straightforwardly from the data and assignments in Table I. The spectra of a number of other O-bonded, complexes have been recorded. All of these spectra are quite similar to those given in Table III and no purpose would be served by tabulating them in full. Instead, we list in Table IV only the frequencies of the SO stretching bands.

TABLE III

INFRARED SPECTRA OF $[\text{Co}(\text{DMSO})_6][\text{CoCl}_4]$, $[\text{Co}(\text{DMSO}-d_6)]_6[\text{CoCl}_4]$, $\text{SnCl}_4 \cdot 2\text{DMSO}$ AND $\text{SnCl}_4 \cdot 2(\text{DMSO}-d_6)$					
Absorption bands		Assignment	Absorption bands		
$[\text{Co}(\text{DMSO})_6][\text{CoCl}_4]$	$[\text{Co}(\text{DMSO}-d_6)]_6[\text{CoCl}_4]$		$\text{SnCl}_4 \cdot 2\text{DMSO}$	$\text{SnCl}_4 \cdot 2(\text{DMSO}-d_6)$	
3002m	2240m	Asymmetrical C-H (C-D) stretch	3030m	2250m	
2906m	2120w	Symmetrical C-H (C-D) stretch	2940m	2130m	
1416m bd	1015s	Asym. $\text{CH}_3(\text{CD}_3)$ deformations	1432s		
				1419s	1019m
			1406m	1012m sh	
1314w	1039m	Sym. $\text{CH}_3(\text{CD}_3)$ def.	1330m	1040w	
1292w				1310w	
1009s sh	819m	$\text{CH}_2(\text{CD}_2)$ rocks	1037s	830m	
999s	775w sh			991s	789w
	760w			948s sh	768m
950vs	970vs	S=O stretch	915 vs bd	929s	914s
714w		Asym. C-S stretch	730m		
		Sym. C-S stretch	685w		

We turn now to the second general class of complexes, those in which, we believe, the sulfoxide is coordinated through the sulfur atom. The compounds $\text{PdCl}_2 \cdot 2\text{DMSO}$ and $\text{PtCl}_2 \cdot 2\text{DMSO}$ appear to be of this type.¹² Their spectra are similar to the

(10) R. Kuhn and H. Trischman, *Ann.*, **611**, 117 (1958).

(11) S. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958).

(12) It should be noted, however, that we have as yet no independent evidence on the structures of these compounds.

TABLE IV
FREQUENCIES OF S-O STRETCHING BANDS IN VARIOUS
DIMETHYL SULFOXIDE COMPLEXES

Compound	Frequency, cm. ⁻¹
Sulfur bonded	
PdCl ₂ ·2DMSO	1116
PtCl ₂ ·2DMSO	1157, 1134
Oxygen bonded	
SnCl ₄ ·2DMSO	915
[Cr(DMSO) ₆](ClO ₄) ₃	928
CrCl ₃ ·4DMSO	935
[Mn(DMSO) ₆](ClO ₄) ₂	955
Mn(ClO ₄) ₂ ·3DMSO·4H ₂ O	954
MnCl ₂ ·3DMSO	950
MnBr ₂ ·3DMSO·6H ₂ O	952
[Fe(DMSO) ₆](ClO ₄) ₂ ·DMSO	940
FeCl ₃ ·2DMSO	933
FeI ₃ ·4DMSO	937
[Co(DMSO) ₆](ClO ₄) ₂	956
CoCl ₂ ·3DMSO	950
CoBr ₂ ·3DMSO	951
CoI ₂ ·6DMSO	948
CoI ₂ ·3DMSO	951
Co(SCN) ₂ ·4DMSO	953
Co(SCN) ₂ ·3DMSO	950
[Ni(DMSO) ₆](ClO ₄) ₂	955
NiCl ₂ ·3DMSO	940
NiBr ₂ ·6DMSO	957
NiBr ₂ ·4DMSO	956
NiBr ₂ ·3DMSO	951
NiI ₂ ·4DMSO	930
Cu(DMSO) ₄ (ClO ₄) ₂	940 v bd
CuCl ₂ ·2DMSO	923
CuBr ₂ ·2DMSO	911
[Zn(DMSO) ₆](ClO ₄) ₂	956
ZnCl ₂ ·2DMSO	952
ZnBr ₂ ·2DMSO	942
CdCl ₂ ·DMSO	950

spectra of O-bonded compounds in the C-H stretching and deformation regions, *i.e.*, down to the ~ 1300 cm.⁻¹ bands. However, as may be seen from the data in Table V for PdCl₂·2DMSO and PdCl₂·2(DMSO-*d*₆), the SO stretching frequency is higher (1116 cm.⁻¹) in the complex than in the free ligand. In the platinum compound there are strong bands at 1157 and 1134 cm.⁻¹ one or both of which must be assigned to S-O stretching. In both the platinum and palladium compounds the four strong to medium intensity bands found between ~ 1025 and ~ 920 cm.⁻¹ may be assigned to CH₃ rocking modes. The bands at 730 and 683 cm.⁻¹ in the palladium compound and at 736 and 689 cm.⁻¹ in the platinum compound may presumably be assigned to C-S stretching frequencies. The behavior of these bands in these S-bonded compounds is in marked contrast to their behavior in the O-bonded compounds. In the latter the C-S stretching bands are generally much weaker (often the symmetric stretch is not observed)

and at lower frequencies, *viz.*, at ~ 715 cm.⁻¹ and, if observable, at ~ 675 cm.⁻¹.

TABLE V
INFRARED SPECTRA OF PdCl₂·2DMSO AND PdCl₂·2(DMSO-*d*₆)

Absorption bands PdCl ₂ ·2-DMSO	Assignment	Absorption bands PdCl ₂ ·2-(DMSO- <i>d</i> ₆)
3010m	Asym. C-H(C-D) stretch	2250s
2920m	Symmetrical C-H(C-D) stretch	2120m
1423m	Asym. CH ₃ (CD ₃) def. } Sym. CH ₃ (CD ₃) def. }	1043w 1029s 1010s
1411m		
1313m		
1298m	S-O stretch	1113s
1116vs		
1022s	CH ₃ (CD ₃) rocks	880w 822vs 787m 778vs
983m		
975w sh		
945m	Asym. C-S stretch	709m
923m		
730m	Sym. C-S stretch	642m
683m		

Experimental

Preparation of Compounds.—The preparations of trimethylsulfoxonium iodide, [(CH₃)₃SO]⁺I⁻, and tri-(methyl-*d*₃)-sulfoxonium iodide have been described previously.² The O-methylsulfoxonium nitrate was prepared by the method of Smith and Winstein.^{11,13} 3.41 g. (20.2 mmoles) of AgNO₃ was dissolved in 10 ml. (116.0 mmoles) of DMSO dried by passing through a column of molecular sieve pellets (type 4A 1/16 inch pellets, Linde Aire Products) and distilled at reduced pressure from powdered molecular sieves. To this mixture, cooled in an ice-bath, were added dropwise 2.84 g. (20.0 mmoles) of CH₃I over a period of about ten minutes. A yellow-white precipitate of AgI was immediately observed. As soon as reaction was complete, the solution was filtered rapidly and the filtrate treated with 100 ml. of anhydrous ether; the mixture formed two layers and the ether layer was decanted. This process was repeated until the oil crystallized to a white solid. This was recrystallized once from chloroform-ether and dried in a vacuum desiccator. The product is extremely hygroscopic and isomerizes in the presence of moisture. The yield was very low. The [(CH₃)₃SO]⁺NO₃⁻ was prepared by treating an aqueous solution of [(CH₃)₃SO]⁺I⁻ with AgNO₃, filtering off the AgI formed and evaporating the resulting solution to dryness.

The complexes of DMSO were prepared by methods described elsewhere.¹ All samples used in the present work were thoroughly analyzed, authentic specimens.

Infrared Spectra.—The infrared spectra were taken on solid samples dispersed in the potassium halide corresponding to the anion present in the complex, pressed into translucent pellets in the usual manner. The complexes containing nitrate or perchlorate ions were studied in potassium bromide and chloride pellets and in hexachlorobutadiene and Nujol mulls. The spectra were taken on a Perkin-Elmer Model 21 recording infrared spectrometer employing a sodium chloride prism. The spectral region between 4000 and 650 cm.⁻¹ was investigated.

Acknowledgment.—We are grateful for generous financial support by the United States Atomic Energy Commission under Contract AT(30-1)-1965 and by the Monsanto Chemical Company through a fellowship to W. D. H., Jr.

(13) S. Smith and S. Winstein, private communication.