[Contribution from the Wm. A. Noyes Laboratory, University of Illinois, Urbana, Ill.]

Donor Properties of Sulfoxides, Alkyl Sulfites, and Sulfones

By Russell S. Drago, Bradford Wayland, and Robert L. Carlson[1]

Received May 2, 1963

The equilibrium constants and enthalpies for formation of adducts of dimethyl sulfoxide, tetramethylene sulfoxide, tetramethylene sulfone, and diethyl sulfite with the acids iodine and phenol have been measured. The donor properties of these materials have been interpreted in terms of inductive and π-bonding effects in the donor molecules. These data are compared with results from similar measurements on other donors commonly employed as nonaqueous solvents. In an earlier article a linear relationship was reported to exist between $-\Delta H$ of formation and the phenol frequency shift $\Delta\nu_{OH}$ for some donor–phenol adducts. The tetramethylene sulfone adduct deviates from this relationship. It is proposed that both oxygens of the sulfone are coordinated to the phenol proton and a proposal for a low frequency shift is based on this model.

Introduction

Recent interest in the unusual properties of sulfoxides and sulfones as aprotic solvents has prompted our investigation of their donor properties toward the acceptors iodine and phenol. We report in this article thermodynamic data for adduct formation of dimethyl sulfoxide (DMSO), tetramethylene sulfoxide (TMSO), and tetramethylene sulfone (TMSO₂), with the Lewis acids iodine and phenol. For the sake of comparison, similar data were obtained for the donors diethyl sulfite and acetonitrile. These results are compared with reported data for other nonaqueous solvents.

In order to interpret trends in the donor properties of the sulfones and sulfoxides, the problem of the extent of sulfur–oxygen π-bonding must be considered. This general problem has been reviewed recently,[2] but no definite conclusions can be drawn because of the ambiguity in interpreting existing data. The main cause of the ambiguity arises from complications introduced by solvent effects. Most of the existing data that bear on this problem have been obtained in water. The donor properties measured in carbon tetrachloride for acetone, sulfoxides, sulfones, and sulfites can be rationalized in terms of changes in π- and σ-bond interactions.

It has been reported that a linear relationship exists between the enthalpy of adduct formation of phenol with several donors and the shift in the O–H stretching vibration of phenol that results from complexation.[3] The data obtained for the adduct of tetramethylene sulfone with phenol do not fit this relationship. This is the first exception reported that we are confident exists and an explanation for the deviation is offered. It is believed that the proton of phenol is simultaneously hydrogen bonded to both oxygens of TMSO₂. This type of interaction is found in some transition metal ion complexes[4] where TMSO₂ behaves as a bidentate ligand.

Experimental

Purification of Reagents.—Dimethyl sulfoxide and tetramethylene sulfoxide were purified by shaking over barium oxide for 4 days and distilling from calcium hydride under reduced pressure. Diethyl sulfite, obtained from the Columbia Chemical Co., was purified by distillation under reduced pressure just prior to using. The center fraction consisting of about 50% of the material was collected for use. Fisher Spectroanalyzed carbon tetrachloride was used without further purification.

Apparatus and Procedures.—The apparatus and procedure employed in making these measurements have been described in previous articles[3,5] along with the methods employed for calculation. The enthalpies are calculated by employing a least squares procedure and errors are reported at the 90% confidence level. Enthalpy results (accurate to ± 0.2 kcal. mole^{-1}) are obtained by

an "enthalpy procedure" previously reported,[3] after the change in molar absorptivity with temperature is evaluated.

Results

Iodine Equilibrium Constants and Enthalpies.— The complex maxima for the blue shift iodine peaks occur at 450 mμ for TMSO and DMSO. The shifted I₂ peak occurred between 475 and 480 mμ in the diethyl sulfite and tetramethylene sulfone complexes. The criteria for selecting the best wave length at which to determine the enthalpies of I₂ complexes have been reported.[5,6] The wave length 550 mμ was selected for the sulfoxides, which show large blue shifts. Enthalpies for the sulfite and sulfone were determined at the complex maxima. Measurements at 450, 460, and 470 mμ gave constant enthalpy values. Ethalpies of formation for the dimethyl sulfoxide and tetramethylene sulfone adducts with phenol were measured at 284 mμ. The TMSO phenol enthalpy was estimated from the reported relationship between the phenol $\Delta\nu_{OH}$ and the ΔH of adduct formation.[3]

Table I

Data and Equilibrium Constants for the Interaction of Some Donors Containing an S–O Group with Iodine
$(T = 25.0°, \lambda = 520 \text{ m}\mu)$

Donor	C_A, mole/l.	C_D, mole/l.	$-(A - A^0)$	$\epsilon_C - \epsilon_A$	K, l./mole
Dimethyl sulfoxide		0.01498	0.165		
	0.00171	.01873	.200	−766	11.6 ± 1.0
		.03746	.329		
		.07492	.518		
Tetramethylene sulfoxide		.00969	.193		
	0.00237	.01212	.237	−651	14.7 ± 0.8
		.02424	.405		
		.04847	.641		
Diethyl sulfite		.4983	.113		
	0.00093	.6229	.137	−846	0.34 ± 0.01
		1.2458	.228		
		2.4916	.351		
Tetramethylene sulfone		0.5447	.211		
	0.00133	0.6809	.244	−553	0.73 ± 0.05
		1.3618	.366		
		2.7236	.509		

Discussion

Table V contains a summary of all the data pertinent to this discussion. The donor sites for many of the adducts in Table V are obvious. It has been established that oxygen is the donor atom in amides.[5] A decrease in the S–O stretching frequency in the iodine and phenol adducts with sulfoxides, compared to free sulfoxide, also indicates oxygen coordination.[7,8] A very slight decrease in the S–O stretching frequency of

(1) Abstracted in part from the Ph.D. thesis of Robert L. Carlson, University of Illinois, 1962.

(2) C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Co., New York, N. Y., 1962.

(3) M. D. Joesten and R. S. Drago, J. Am. Chem. Soc., **84**, 3817 (1962); R. M. Badger and J. H. Bauer, J. Chem. Phys., **5**, 839 (1937).

(4) C. H. Langford and P. O. Langford, Inorg. Chem., **1**, 184 (1962).

(5) R. L. Carlson and R. S. Drago, J. Am. Chem. Soc., **84**, 2320 (1962).

(6) R. S. Drago, R. L. Carlson, N. J. Rose, and D. A. Wenz, ibid., **83**, 3572 (1961).

(7) R. S. Drago and D. W. Meek, J. Phys. Chem., **65**, 1446 (1961), and references contained therein.

(8) W. D. Horrocks, Jr., and F. A. Cotton, Spectrochim. Acta, **17**, 134 (1961).

TABLE II

DATA AND ENTHALPY CHANGES FOR THE INTERACTION OF SULFOXIDES, DIETHYL SULFITE, AND TETRAMETHYLENE SULFONE WITH IODINE

Donor	C_A, mole/l.	C_D, mole/l.	$-(A - A^0)$	$\epsilon_C - \epsilon_A$	λ, mμ	K, l./mole	Temp., °C.	$-\Delta H$, kcal./mole
Dimethyl sulfoxide	0.00176	0.0313	0.308			12.37	23.4	
	.00174	.0310	.273			10.66	28.9	
	.00173	.0308	.241	−638	550	9.20	35.4	4.4 ± 0.3
	.00172	.0306	.219			8.27	40.6	
	.00171	.0304	.195			7.25	46.1	
Tetramethylene sulfoxide	.00237	.0179	.334			14.90	24.8	
	.00236	.0178	.308			13.57	29.2	
	.00235	.0177	.271	−686	550	11.75	35.0	4.4 ± 0.3
	.00233	.0176	.247			10.63	39.5	
	.00232	.0175	.220			9.39	45.1	
Diethyl sulfite	.000986	1.248	.242			0.347	23.5	
	.000983	1.245	.233			.331	27.3	
	.000975	1.234	.221	812	470	.314	32.6	2.2 ± 0.3
	.000971	1.229	.211			.297	36.2	
	.000969	1.226	.208			.293	38.3	
	.000971	1.217	.194			.272	44.1	
Tetramethylene sulfone	.00133	0.545	.279			.731	25.0	
	.00132	.540	.259	735	470	.673	32.1	2.2 ± 0.3
	.00131	.531	.239			.621	39.3	
	.00130	.531	.223			.573	45.5	

TABLE III[a]

DATA AND EQUILIBRIUM CONSTANTS FOR THE INTERACTION OF PHENOL WITH A SULFONE AND A SULFOXIDE ($T = 25.0°$, $\lambda = 284$ mμ)

Donor	C_A, mole/l.	C_D, mole/l.	$A - A^0$	$\epsilon_C - \epsilon_A$	K, l./mole
Dimethyl sulfoxide		0.003094	0.357		
	0.000727	.006188	.536	1435	182 ± 1
		.015470	.763		
Tetramethylene sulfone		0.008878	.260[b]		
	0.002996	.022196	.547	706	17.1 ± 0.7
		.044392	.860		

[a] C_A is the concentration of acid; C_D is the concentration of donor; $A - A^0$ is the absorbance of the complex minus the absorbance of the acid; $\epsilon_C - \epsilon_A$ is the difference in the molar absorptivity between the complex and acid. All measurements were made in carbon tetrachloride. [b] $A - A^0$ corrected for small absorbance due to tetramethylene sulfone (ϵ_D = 0.44 at 284 mμ).

TABLE IV[a]

DATA AND ENTHALPY CHANGES FOR THE INTERACTION OF PHENOL WITH DIMETHYL SULFOXIDE AND TETRAMETHYLENE SULFONE ($\lambda = 284$ mμ)

Donor	C_A, mole/l.	C_D, mole/l.	$A - A^0$	$\epsilon_C - \epsilon_A$	K, l./mole	Temp., °C.	$-\Delta H$, kcal./mole
Dimethyl sulfoxide	0.00727	0.006188	0.536		183.0	25.0	
	.00725	.006169	.514		169.3	27.3	
	.00722	.006145	.480	1435	149.5	30.7	6.5 ± 0.2
	.00715	.006083	.422		121.5	36.8	
Tetramethylene sulfone	.001913	.02527	.408[b]		17.53	25.0	
	.001904	.02516	.381		15.91	28.4	
	.001895	.02503	.350	706	14.44	32.5	4.9 ± 0.3
	.001889	.02496	.331		13.48	34.8	
	.001884	.02488	.313		12.59	37.3	

[a] Footnotes the same as in Table III.

density into the ring than a methyl group. This occurs by a conjugative mechanism in which lone pair electrons on the oxygen form a π-bond with carbon, placing electron density on the o- and p-positions of the ring. The substituent constant for a m-substituted ethoxyl group indicates it is electron withdrawing relative to a methyl group. The conjugative mechanism is not as important in this position and the withdrawal of electron density by the electronegative oxygen is more important than conjugation effects. Since diethyl sulfite is a poorer donor than dimethyl sulfoxide, the ethoxyl group must be withdrawing electron density from the sulfur. It can be concluded that sulfur-oxygen π-bonding involving the d-orbitals of sulfur and the ethoxyl group is much less effective than carbon-oxygen π-bonding in the p-position of a phenyl ring. Because of poorer π-bonding the electronegativity of oxygen results in the withdrawal of electron density

the sulfite adduct with iodine is consistent with coordination on the sulfoxyl oxygen and a weak interaction. This conclusion is uncertain, but if the acid coordinates on the "ethoxyl" oxygen the sulfoxyl oxygen would be an even poorer donor and the following discussion is still pertinent.

A comparison of the donors dimethyl sulfoxide and diethyl sulfite shall be considered first. The Hammett substituent constants indicate that an ethoxyl group in the p-position of a benzene ring releases more electron

from sulfur, which decreases the donor properties of the sulfoxyl oxygen. If π-bonding were the dominant term the sulfoxyl oxygen would be a strong donor.

The stronger donor ability of the sulfoxides than acetone is also consistent with less effective sulfur-oxygen π-bonding. The valence state electronegativity for tetrahedral sulfur[9] (3.21) is greater than that for a

(9) This value represents a lower limit for it pertains to sulfur with two lone pairs which is less electronegative than a similarly hybridized sulfur in the sulfoxide with only one lone pair.

TABLE V

SUMMARY OF PERTINENT THERMODYNAMIC DATA FOR THE
FORMATION OF PHENOL AND IODINE ADDUCTS

Donor	Acid	K, l./mole	$-\Delta H$, kcal./mole	Ref.
$(CH_3)_2CO^a$	I_2	0.85 (25°)		10[a]
$(CH_2)_4SO$	I_2	14.7 ± 0.8 (25°)	4.4 ± 0.3	10
$(CH_3)_2SO$	I_2	11.6 ± 1.0 (25°)	4.4 ± .3	10
$(CH_2)_4SO_2$	I_2	0.73 ± 0.05 (25°)	2.2 ± .3	10
$(CH_3O)_2SO$	I_2	0.34 ± 0.01 (25°)	2.2 ± .3	10
$HCON(CH_3)_2$	I_2	2.9 ± 0.2 (25°)	3.7 ± .3	11
$CH_3CON(CH_3)_2$	I_2	6.9 ± 0.2 (25°)	4.0 ± .1	12
$(C_2H_5)_2O$	I_2	1.16 (20°)	4.2	13
$(C_2H_5)_2S$	I_2	210 (20°)	7.8	14
CH_3CN	I_2	0.40 ± 0.03 (25°)	2.3 ± .3	10, 15
C_6H_6	I_2	0.15 (25°)	1.5	16, 17
$(CH_3)_2CO$	C_6H_5OH	13.5 ± 1.0 (25°)	3.3 ± .5	2
$(CH_2)_4SO$	C_6H_5OH		7.0	18
$(CH_3)_2SO$	C_6H_5OH	182 ± 1 (25°)	6.5 ± .2	10
$(CH_2)_4SO_2$	C_6H_5OH	17.1 ± 0.7 (25°)	4.9 ± .3	10
$HCON(CH_3)_2$	C_6H_5OH	64 ± 1 (25°)	6.1 ± .2	2
$CH_3CON(CH_3)_2$	C_6H_5OH	134 ± (25°)	6.4 ± .2	19
$(C_2H_5)_2O$	C_6H_5OH		5.0	20
$(C_2H_5)_2S$	C_6H_5OH		4.6	
CH_3CN	C_6H_5OH	5.0 ± 0.2 (25°)	3.3 ± .5	2
C_6H_6	C_6H_5OH		1.5	18

[a] Due to the formation of triiodide, indicative of a more complex reaction, the acetone-I_2 enthalpy could not be determined accurately.

trigonal carbon (2.75).[21] If electronegativity were the sole effect operative, acetone would be a stronger donor than sulfoxide. The stronger donor properties of sulfoxide can be attributed to less effective sulfur–oxygen π-bonding than the carbon–oxygen π-bonding in acetone. Less effective π-bonding in the sulfoxide results in more electron density residing on the sulfoxyl oxygen, and as a result it is a stronger donor than acetone. The different properties discussed above are thus attributed to less effective π-bonding between second and third row elements than between two second row elements, presumably because of less effective π-overlap in the former case.

It is informative to compare the donor properties of diethyl sulfide, diethyl ether, tetramethylene sulfoxide, and tetramethylene sulfone. As can be seen from the data in Table V, diethyl sulfide is a better donor toward iodine than diethyl ether, but the reverse order of donor strengths applies toward the acid phenol. In the interaction with iodine (a very polarizable acid with no dipole moment) the ease with which the lone pair on the donor can be distorted is an important property of the donor affecting the magnitude of the interaction. Toward phenol, a polar acid, the lone pair dipole moment of the donor, in a configuration similar to that in the adduct, becomes an important parameter. Keeping this in mind it is interesting to note that both iodine and phenol coordinate on the oxygen atom of sulfoxide instead of the sulfur. Compared to dimethyl sulfide, considerable electron density has been drained off the sulfur of sulfoxide by the electronegative oxygen atom

(10) This work.

(11) R. S. Drago, D. A. Wenz, and R. L. Carlson, *J. Am. Chem. Soc.*, **84**, 1106 (1962).

(12) R. S. Drago, R. L. Carlson, N. J. Rose, and D. A. Wenz, *ibid.*, **83**, 3572 (1961).

(13) M. Tamres and M. Brandon, *ibid.*, **82**, 2134 (1960).

(14) H. Tsubomura and R. P. Lang, *ibid.*, **83**, 2085 (1961).

(15) Subsequent to our measurements values of K = 0.42 ± 0.005 and $-\Delta H$ = 1.9 ± 0.6 were reported by W. B. Person, W. C. Golton, and A. I. Popov, *J. Am. Chem. Soc.*, **85**, 891 (1963).

(16) L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 4500 (1952).

(17) R. M. Keefer and L. J. Andrews, *ibid.*, **77**, 2164 (1955).

(18) Enthalpies determined by the O–H stretching frequency shift method reported in ref. 3; $\Delta H = 0.016\Delta\gamma_{OH} + 0.64$.

(19) M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 2037 (1962).

(20) R. West, reported at the 140th National Meeting of the American Chemical Society, St. Louis, Mo., March, 1961.

(21) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

and by rehybridization of the sulfur atom. No detectable sulfur-coordinated complex is observed with iodine in excess sulfoxide, so the equilibrium constant for such a complex must be orders of magnitude less than for the oxygen complex.

In the sulfone, the weakly basic pair of sulfur electrons present in the sulfoxide is bonded to an oxygen. If we view this as coordination of the sulfur lone pair by oxygen, the net effect would be to drain electron density off the sulfur and from the sulfur oxygen bond. An increase in the S–O stretching frequency results. This causes a decrease in electron density on the sulfone oxygens relative to the sulfoxide oxygen and an appreciable decrease in electron density on the sulfur in the sulfone. As a result the sulfone is a poorer donor than sulfoxide. In addition to the decrease in donor properties by this redistribution of electron density in the σ-system, a decrease is also expected from more effective oxygen to sulfur π-bonding in the sulfone because of the d-orbital contraction[22] that occurs as electron density is removed from sulfur. The above effects are also manifested in the sulfur–oxygen stretching force constants in sulfoxides and sulfones. A value of 6.54 × 10^{5} dynes cm.$^{-1}$ has been reported for the S–O force constant in dimethyl sulfoxide[8] and 9.86 × 10^{5} dynes cm.$^{-1}$ for sulfones.[23]

The donor strength of the sulfone toward the polarizable acid iodine is of the same order of magnitude as that of the weak donor benzene. Since the sulfone has a high dipole moment, the low heat indicates that the electron density in the molecule is not easily distorted in keeping with a high formal charge on sulfur. This is equivalent to saying that the sulfone forms only weak covalent bonds with iodine. The S–O stretching frequency of the coordinated sulfone in both the iodine and phenol adducts occurs at about the same frequency as in the uncoordinated sulfone. This also indicates very little polarization of the electron density on the oxygen upon coordination. The low equilibrium constant and heat of formation of the acetonitrile–iodine adduct can be similarly rationalized.

As indicated by the data in Table V, the donor properties of dimethyl sulfoxide and N,N-dimethylacetamide are very much alike. The equilibrium constants for the sulfoxide are slightly greater. There is no detectable difference in the enthalpy of formation of adducts of dimethyl sulfoxide and tetramethylene sulfoxide. The equilibrium constant for formation of the dimethyl sulfoxide adduct is slightly lower. The similarity in the coordinating abilities of these donors toward nickel-(II) is also reflected in the similarity in the reported Dq-values of these materials as ligands.[24,25] Values of 769, 773, and 775 cm.$^{-1}$ are reported for DMA, DMSO, and TMSO, respectively. Since the dielectric constants of DMA and DMSO are also similar (38.9, 48.9), one would expect them to have many similarities as nonaqueous solvents. Ionization will be facilitated to a slightly greater extent in DMSO. A similar conclusion could be made regarding expected similarity in solvent behavior of acetonitrile and tetramethylene sulfone. However the possibility that the sulfone can behave as a bidentate ligand will lead to appreciable differences.

The shift of the phenol O–H stretching frequency upon adduct formation has been shown to be linearly

(22) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 332 (1954); D. P. Craig and C. Zauli, *J. Chem. Phys.*, **37**, 601, 609 (1962).

(23) K. Fujimori, *Bull. Chem. Soc. Japan*, **32**, 1374 (1959).

(24) D. W. Meek, R. S. Drago, and T. S. Piper, *Inorg. Chem.*, **1**, 285 (1962).

(25) R. S. Drago, D. W. Meek, M. D. Joesten, and L. LaRoche, *ibid.*, **2**, 124 (1963).

related to the enthalpy of adduct formation for a wide variety of donors with phenol.[3] The DMSO–phenol adduct obeys this relationship very well. All of the bases studied in determining the $\Delta\nu_{OH}$ vs. ΔH relationship form linear or near linear hydrogen bonds, i.e., the angle θ in Fig. 1 is 180°. The anomalously low O–H stretching frequency shift for the phenol–TMSO$_2$ adduct suggests that the bonding or geometry of the sulfone adduct differs from the adducts used in determining this relationship. Tetramethylene sulfone has recently been reported to act as a bidentate ligand in metal ion complexes.[4] We tentatively propose a similar model for the phenol–TMSO$_2$ adduct which places the acidic phenol hydrogen between and equidistant from the two sulfonic oxygens (Fig. 1). Using
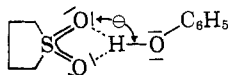

Fig. 1.—Proposed structure of the adduct between TMSO$_2$ and phenol.

this model the phenolic oxygen–sulfonic oxygen lone pair electron–electron repulsions are enhanced, but this repulsion term must be more than compensated for by the phenol dipole interacting which each of two oxygen lone pair dipoles maximizing electrostatic interaction. The hydrogen bond in the structure proposed in Fig. 1 is not linear as indicated by the angle θ, which is 180° in a linear hydrogen bond. The nonlinear hydrogen bonds suggested for the sulfone–phenol adduct must be relatively ineffective in polarizing the O–H bond when compared to a linear hydrogen bond. This may be the result of reduced lone pair–

hydrogen overlap. The repulsions of nonbonding lone pair electrons on the sulfone and phenol prevent the overlap from being as great as in a linear hydrogen bond. There are unusually large contributions to the heat of interaction in this adduct from the electrostatic term and this accounts for the deviation of this adduct from the ΔH–$\Delta\nu_{O-H}$ correlation.

The deviation of the tetramethylene sulfone adduct from the $-\Delta H$ vs. $\Delta\nu_{O-H}$ correlation may also be in part due to a low frequency shift resulting from the nonlinearity of the hydrogen bond. As the phenolic O–H distance increases during the stretching vibration in a linear hydrogen-bonded adduct, overlap of the donor lone pair electrons and the proton increases, partially compensating for the decreased overlap in the phenolic O–H bond. This results in a lower energy and lower frequency for the O–H stretching vibration than would be obtained in the absence of this effect. In a bent hydrogen bond, the proton moves at an angle to the donor lone pair during the O–H stretching vibration (see Fig. 1) and lone pair proton overlap is not increased as much when the bond is stretched as in a linear hydrogen bond. As a result the energy of the vibration is decreased less and the frequency shift is smaller for a bent bond than for a linear bond.

These two reasons for the deviation require that there be significant contributions to the frequency shift from covalency.