Donor Properties of Some Sulfur Compounds[1]

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Evidence is presented to indicate that the compounds $CH_3C(S)N(CH_3)_2$, $(CH_3)_2NC(S)N(CH_3)_2$, and $C_6H_5SCH_3$ form sulfur coordinated adducts with iodine and phenol, while $CH_3C(O)SCH_3$ forms oxygen coordinated adducts. The thermodynamic data for formation of these adducts in CCl_4 solution are reported, and the donor properties are interpreted in terms of the electronic structure of the donor and the nature of the donor–acceptor interaction. These interpretations are substantiated by the C^{13} proton n.m.r. coupling constants. Evidence is presented to indicate substantial C–S π-bonding in CH_3COSCH_3.

Introduction

In contrast to the large amount of quantitative data available for oxygen donors, very little information is available for sulfur donors. Thermodynamic data for adduct formation between dialkyl sulfides and the acids I_2,[2–4] BH_3,[5,6] BF_3,[6] and BCl_3[6] have been reported. Similar studies have been carried out with a series of saturated cyclic sulfides.[7,8] Adducts formed by iodine and diethyl disulfide,[3,4] $C_2H_5S_2C_2H_5$, and those formed by halogens and interhalogens with the phosphine sulfides[9] have been studied quantitatively.

The sulfur donors studied interact more strongly than the analogous oxygen donors with the acids I_2 and BH_3 but less strongly with BF_3 and BCl_3.

In previous articles,[10] the magnitude of the donor–acceptor interaction has been rationalized in terms of the ease with which the electronic structures at the reactive sites of the acceptors and donors can be distorted. Donors and acceptors that are both easily distorted form stronger adducts with each other than with acids and bases that are less easily distorted. Certain acceptors are polar and not so easily distorted. The magnitude of the interaction with this type of acceptor is more sensitive to the polar nature of the donor, and oxygen donors are often better than the analogous sulfur donors. Iodine is an example of a distortable acid, while the hydrogen bonding interaction of phenol is found to be quite sensitive to the polarity of the donor. The enthalpy of formation of the adducts formed between sulfur or oxygen donors and the acids I_2, BH_3, BF_3, and BCl_3 can be rationalized with these arguments. Data on a large number of other systems have also been interpreted[11] by similar arguments. Acids or bases whose electronic structure is easily distorted are referred to as *soft* and those which are not are referred to as *hard*.

With these considerations in mind it was of interest to investigate and compare the magnitude of the in-teraction of the Lewis acids iodine and phenol with the donors N,N-dimethylthioacetamide, $CH_3C(S)N(CH_3)_2$, tetramethylthiourea, $(CH_3)_2NC(S)N(CH_3)_2$, S-methyl thioacetate, $CH_3C(O)SCH_3$, and phenyl methyl sulfide, $C_6H_5SCH_3$. This comparison also demonstrates the effects of substituents on the donor properties of sulfur.

Experimental

Preparation and Purification of Materials.—Fisher Spectranalyzed carbon tetrachloride was used without further purification. The purification procedure for iodine has been reported.[12] Baker and Adamson reagent grade phenol was distilled at atmospheric pressure. The fraction boiling at 182° was collected.

Tetramethylthiourea was prepared by the regulated thermal decomposition of bis(dimethylthiocarbamyl) disulfide as described by Shaw and Walker.[13] This was accomplished by heating the starting material under air reflux for several hours. The resulting mass was recrystallized three times from water. *Anal.* Calcd. for $C_5H_{12}N_2S$: C, 45.41; H, 9.15; N, 21.19. Found: C, 45.62; H, 9.16; N, 21.13.

N,N-Dimethylthioacetamide was synthesized from N,N-dimethylacetamide and phosphorus pentasulfide according to the general procedure given by Hofmann.[14a] The compound was recrystallized from water. *Anal.* Calcd. for C_4H_9NS: C, 46.56; H, 8.79; N, 13.58. Found: C, 46.40; H, 8.62; N, 13.59.

Phenyl methyl sulfide was prepared from C_6H_5SNa and CH_3I.[14b] The colorless liquid was distilled at atmospheric pressure, b.p. 192–196°, and redistilled at reduced pressure, b.p. 65.0–65.5° (5 mm.). *Anal.* Calcd. for C_7H_8S: C, 67.69; H, 6.49. Found: C, 67.58; H, 6.64.

The apparatus and procedure for determining and calculating equilibrium constants have been reported previously.[15] The procedure employed for accurate determination of the enthalpies has also been described.[15] The infrared spectra of donor–iodine systems were obtained with a Perkin-Elmer Model 21 double-beam spectrometer employing sodium chloride optics. The O–H stretching frequency shifts of the donor–phenol systems were obtained on a Beckman Model IR-7 double-beam spectrometer with a fore-prism–grating optical system. Nuclear magnetic resonance spectra were obtained using a Varian Model A-60 n.m.r. spectrometer. Tetramethylsilane was used as an internal reference, and all spectra were recorded at room temperature.

Results

The data employed for calculation of equilibrium constants of the systems studied are contained in Table I.

Enthalpies were determined by measuring the change in absorbance of a single solution as a function of temperature. Readings were taken about every 3° over the temperature range 25.0 to 40.0°. Enthalpies were calculated from a least-squares determination of

(1) Abstracted in part from the Ph.D. Theses of Robert J. Niedzielski and Richard L. Middaugh, University of Illinois, Urbana, Ill.

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(7) J. D. McCullough and D. Mulvey, *J. Am. Chem. Soc.*, **81**, 1291 (1959).

(8) M. Tamres and S. Searles, Jr., *J. Phys. Chem.*, **66**, 1099 (1962).

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(13) W. H. R. Shaw and D. G. Walker, *ibid.*, **79**, 4329 (1957).

(14) (a) A. W. Hofmann, *Ber.*, **11**, 338 (1878); (b) E. Bourgeois and A. Abraham, *Rec. trav. chim.*, **30**, 407 (1911).

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

TABLE I

EQUILIBRIUM CONSTANT DETERMINATIONS

Donor	λ, mμ	Temp., °C.	C_1, M^a	C_D, M^b	$-(A - A^0)^c$	$\epsilon_C - \epsilon_1{}^d$	K, l. mole^{-1}
$(CH_3)_2NC(S)N(CH_3)_2$	550	25.0	0.00100	0.000106	0.044		
				.000212	.087	−473	7840
				.000424	.168		
			.000946	.000200	.084		
				.000399	.163	−490	8400
				.000799	.293		
			.000993	.000230	.097		
				.000460	.191	−490	7580
				.000920	.332		
$CH_3C(S)N(CH_3)_2$	550	25.0	.000482	.000116	.022	−578	1100
				.000464	.075		
			.000208	.000224	.018	−472	1200
				.000448	.031		
			.000214	.000216	.019	−510	1180
				.000432	.033		
			.000199	.000218	.018	−488	1250
				.000436	.031		
			.000164^e	.000120	.045	−485	1250
				.000481	.138		
$C_6H_5SCH_3$	550	25.0	.000934	.0499	.140		
				.0998	.211	−475	9.22
				.1997	.289		
	530	25.0	.000934	.0499	.163		
				.0998	.248	−555	9.24
				.1997	.336		
	550	25.0	.000890	.0403	.114		
				.0806	.178	−464	9.48
				.1610	.250		
	550	45.4	.000869	.0393	.068		
				.0787	.113	−411	5.98
				.1572	.174		
	550	25.0	.001002	.0677	.154		
				.1354	.222	−403	9.11
				.2709	.288		

^{a} Total concentration of iodine. ^{b} Total concentration of base. ^{c} Absorbance of 1 cm. of adduct solution measured against a blank, consisting of C_1 molar iodine in CCl$_4$. ^{d} $\epsilon_C - \epsilon_1$ is the difference in molar absorptivity of the complex and iodine. ^{e} 5-cm. cells were employed.

the slope of a plot of log K vs. $1/T$. The donor concentrations were about 0.0002, 0.001, and 0.16 M for N,N-dimethylthioacetamide, tetramethylthiourea, and phenyl methyl sulfide, respectively. In each case, the iodine concentration was about 0.001 M. Values of −500, −490, and −470, respectively, were employed for the $\epsilon_C - \epsilon_1$ values at 550 mμ. The enthalpies determined are listed in Table II along with other data pertinent to the discussion.

The enthalpies for the interaction of these donors with phenol are estimated from the magnitude of the infrared frequency shift of phenol upon complexation by using the relationship

$$-\Delta H \text{ (kcal. mole}^{-1}) = 0.016\Delta\nu_{O-H} + 0.63$$

This relationship has been tested for phenol on a large number of donor systems.[16] It is interesting to point out that the heat of adduct formation of the $(EtO)_3PS$–phenol adduct is predicted to be −3.4 kcal. mole^{-1} on the basis of the frequency shift, and a value of −3.2 kcal. mole^{-1} was experimentally determined.[17]

(16) M. D. Joesten and R. S. Drago, J. Am. Chem. Soc., **84**, 3817 (1962).

The infrared spectra of $(CH_3)_2NC(S)N(CH_3)_2$ and its iodine adduct were obtained for solutions 0.07 M in donor and 0.08 M in iodine in CHCl$_3$ and in CHBr$_3$. At these concentrations, about 99% of the donor is complexed. The regions 1150 to 1200 cm.$^{-1}$, 1065 to 1085 cm.$^{-1}$, and below 870 cm.$^{-1}$ were not accessible due to strong solvent absorption. The spectral data are given in Table III.

The chemical shifts, τ, obtained from the n.m.r. spectra of the compounds employed in this study are summarized in Table IV along with the $J_{C^{13}H}$ coupling constants.

The n.m.r. spectrum of $(CH_3)_2NCSN(CH_3)_2$ was found to exhibit a single sharp peak, while the spectrum of $CH_3C(S)N(CH_3)_2$ contains three sharp peaks, two of which are closely spaced. The two closely spaced peaks are attributed to nonequivalent N-methyl groups. The nonequivalence arises because of the barrier to rotation about the C–N bond. Similar results have been reported for the oxygen analogs of these two compounds (amides and ureas).[18] The explana-

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TABLE II

Donor	K_{298}, l. mole^{-1}	$-\Delta H$,[a] kcal. mole^{-1}	$\Delta\nu_{O-H}$, cm.$^{-1}$	$-\Delta H$,[b] kcal. mole^{-1}
$(C_2H_5)_2O^k$	0.97	4.3	279[d]	5.1
$(C_2H_5)_2S^c$	210	7.8	250[e]	4.6
$(C_2H_5)_2S_2{}^c$	5.6	4.6	...	...
$CH_3C(O)N(CH_3)_2{}^f$	6.9 ± 0.2	4.0 ± 0.1	342[g]	6.1
$C_6H_5OCH_3$			165[e]	3.3
$C_6H_5SCH_3$	9.2 ± 0.1	6.1 ± 0.2	170	3.4
$CH_3C(O)SCH_3{}^h$	0.73 ± 0.01	3.2 ± 0.1	162[h]	3.2
$CH_3C(S)N(CH_3)_2$	1190 ± 40	9.5 ± 1.5	301	5.5
$(CH_3)_2NC(S)N(CH_3)_2$	8000 ± 200	10.5 ± 0.5	317	5.7
$(C_6H_5)_3PS^i$	106			
$(C_6H_{11})_3PS^i$	1820			
$(CH_3)_3PS^i$	604			
$(n\text{-}C_4H_9)_3PS^i$	59			
$(C_2H_5O)_3PS^j$	10.0	5.9	172	3.4

[a] Uncertainties are calculated at the 95% confidence level. [b] Uncertainty is ±0.5 kcal. at the 90% confidence level. [c] See ref. 3. [d] R. West, reported at 139th National American Chemical Society Meeting, St. Louis, Mo., March, 1961. [e] Private communication, B. Wayland, University of Illinois. [f] R. S. Drago, R. L. Carlson, N. J. Rose, and D. A. Wenz, *J. Am. Chem. Soc.*, **83**, 3572 (1961). [g] See ref. 16. [h] See ref. 18. [i] See ref. 9. [j] See ref. 17. [k] P. A. D. de Maine, *J. Chem. Phys.*, **26**, 1192 (1957).

TABLE III

INFRARED SPECTRA OF TETRAMETHYLTHIOUREA AND ITS ADDUCT WITH IODINE IN $CHCl_3$ AND $CHBr_3{}^a$

ν, cm.$^{-1}$	
$(CH_3)_2NC(S)N(CH_3)_2$	$(CH_3)_2NC(S)N(CH_3)_2-I_2$
1512 (s)	1550 (s)
1490 (sh)	1495 (m)
1465 (m)	1465 (m)
1440 (w)	1440 (w)
1405 (vw)	1412 (w)
	1390 (s)
1375 (s)	1375 (vs)
1360 (s)	
1272 (m)	1265 (m)
1215 (m)	1205 (m)
1140 (s)	1155 (m)
1115 (s)	1110 (vs)
1095 (s)	1095 (s)
1055 (w)	1055 (w)
880 (m)	870 (m)

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

tion proposed to account for the difference in the barriers of the amide and urea systems[18] also applies to the sulfur analogs.

The n.m.r. spectrum of S-methyl thioacetate has been reported and discussed previously.[19]

Discussion

The first concern is with the position of coordination in the donors, CH_3COSCH_3, $CH_3CSN(CH_3)_2$, and

(18) R. L. Middaugh, R. S. Drago, and R. J. Niedzielski, *J. Am. Chem. Soc.*, **86**, 388 (1964).

(19) R. L. Middaugh and R. S. Drago, *ibid.*, **85**, 2575 (1963).

$(CH_3)_2NC(S)N(CH_3)_2$. Iodine and phenol most probably coordinate to the oxygen of $CH_3C(O)SCH_3$ as evidenced by a slight decrease in wave number for the carbonyl stretching vibration in the adduct compared to the free donor (1688 compared to 1696 cm.$^{-1}$).[20]

Infrared spectroscopy is, at present, of little help in determining the coordination position in $(CH_3)_2NC(S)N(CH_3)_2$ and $CH_3CSN(CH_3)_2$. The difficulties encountered in attempted assignments of the C=S stretching vibration have been reviewed.[21] The infrared absorption bands of $(CH_3)_2NC(S)N(CH_3)_2$ near 1500, 1375, and 1130 cm.$^{-1}$ were found to undergo changes in intensity and frequency (see Table III). The infrared spectrum of the $CH_3C(S)N(CH_3)_2-I_2$ adduct was not obtained, due to decomposition of the solutions.

TABLE IV

CHEMICAL SHIFTS AND CARBON-13 PROTON COUPLING CONSTANTS

	τ, p.p.m.[a]	$J_{C^{13}H}$, c.p.s.
$(CH_3)_2NC(S)N(CH_3)_2$	6.94	139
$^aCH_3C(S)N(CH_3)_2{}^b$	a, 7.43	130
	b, 6.58, 6.68	138, 138
$^aC_6H_5SCH_3{}^b$	a, 2.78 (multiplet)	
	b, 7.57	139
$^aCH_3C(O)N(CH_3)_2{}^b$	a, 8.03	128
	b, 6.98, 7.17	138, 138
$(CH_3)_2NH^b$	7.65	132
$C_6H_5N(CH_3)_2{}^c$		135 (CH_3)
$^aHC(O)N(CH_3)_2{}^{b\,c,d}$		a, 192
		b, 138
$^aCH_3C(O)NHCH_3{}^b$		a, 128
		b, 137.5
$CF_3C(O)N(CH_3)_2$	6.84, 6.96	140.5, 140.5
$(CH_3)_2NC(O)N(CH_3)_2$	7.27	137
$(CH_3)_2NC(O)NH_2$	6.62[e]	139[e]
$^aCH_3OC(O)N(CH_3)_2{}^b$	a, 6.40	146
	b, 7.13	137.5
$^aCH_3SC(O)N(CH_3)_2{}^b$	a, 7.73	142.5
	b, 7.00	139.5
$(CH_3)_2S^c$		138
CH_3SH^c		138
$(CH_3)_2SO^b$		138
$(CH_3)_2SO_2{}^c$		140[e]
$^aCH_3C(O)SCH_3{}^{b\,f}$	a, 7.70	131
	b, 7.73	143

[a] Chemical shift in CCl_4 solution relative to internal tetramethylsilane at 10.00 p.p.m. [b] See ref. 23a. [c] See ref. 23b. [d] See ref. 23c. [e] Aqueous solution. Chemical shift given is relative to external tetramethylsilane at 10.00 p.p.m., with no correction for bulk magnetic susceptibility. [f] See ref. 19.

Indirect arguments can be presented to support sulfur coordination for the donors $(CH_3)_2NC(S)N(CH_3)_2$ and $CH_3C(S)N(CH_3)_2$. The N-methyl resonance in the n.m.r. spectrum of $CH_3CSN(CH_3)_2$ is found to consist of a doublet, as is the case for $CH_3CON(CH_3)_2$, indicative of appreciable C–N π-bonding. In the case of amides this interaction decreases the donor tendencies of the nitrogen to such an extent that oxygen coordina-

(20) This effect has been discussed for N,N-dimethylacetamide: C. D. Schmulbach and R. S. Drago, *ibid.*, **82**, 4484 (1960).

(21) L. J. Bellamy in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, Oxford, 1961, p. 47.

tion occurs. Even in tetramethylurea, the oxygen is the donor atom toward iodine and phenol. By analogy, an appreciable decrease in the donor strength of the nitrogen would also be expected in both $CH_3C(S)N(CH_3)_2$ and $(CH_3)_2NCSN(CH_3)_2$ compared to dimethylamine. The heat of adduct formation of dimethylamine with iodine is -9.8 kcal. mole^{-1},[22] and that of diethyl sulfide, -7.8 (Table II). The large heat of formation of the iodine adducts with $CH_3C(S)N(CH_3)_2$ and $(CH_3)_2NCSN(CH_3)_2$ is taken as an indication of sulfur coordination. Secondly, the reversal in donor strength of $CH_3C(S)N(CH_3)_2$ and $CH_3CON(CH_3)_2$ toward iodine and phenol is similar to the reversal observed for other sulfur and oxygen donors toward these Lewis acids. These considerations support assignment of the coordination position to sulfur in these donors.

The above conclusion is reinforced by the carbon-13 proton coupling constants for the N-methyl groups in $CH_3C(S)N(CH_3)_2$ and $(CH_3)_2NC(S)N(CH_3)_2$ (see Table IV). The data in Table IV show that $J_{C^{13}H}$ for an N-methyl group in an amide is about 138, much higher than the value for $(CH_3)_2NH$ or $(CH_3)_2NC_6H_5$. It is interesting that the coupling constants in the substituted ureas are approximately the same as for the amides. The magnitude of $J_{C^{13}H}$ reflects the electron-withdrawing power of the group attached to the methyl group by showing the extent to which the hybridization of the carbon atom is affected by the substituent.[23] The values 139 and 138 c.p.s. for $(CH_3)_2NC(S)N(CH_3)$ and $CH_3C(S)N(CH_3)_2$ show that the nitrogen atoms in these donors are similar to those in $(CH_3)_2NC(O)N(CH_3)_2$ and $CH_3C(O)N(CH_3)_2$, and quite different from that in $(CH_3)_2NH$. The effect of the $C=S$ group on the nitrogen is similar to that of the $C=O$ group, which weakens drastically the donor ability of the nitrogen. On this basis, a significantly weaker interaction than 9 kcal. with iodine would be expected if the nitrogen were the donor atom in $(CH_3)_2NC(S)N(CH_3)_2$ and $CH_3C(S)N(CH_3)_2$.

Recently, proton n.m.r. spectra of $CH_3C(S)NH_2$, $CH_3C(S)NHC_6H_5$, $H_2NC(S)NH_2$, and $CH_3NHC(S)NH_2$ in fluorosulfonic acid have been interpreted to indicate that protonation occurs on the sulfur atom in each case.[24] This is in accord with the above discussion and further supports the proposal that the interactions of similar donors with the hydrogen bonding acid phenol and with iodine would be through the sulfur.

When the enthalpies of adduct formation between iodine and the sulfur donors $(C_2H_5)_2S$, $(C_2H_5S)_2$, and $C_6H_5SCH_3$ are plotted against the sum of the inductive substituent constants, σ_I,[25,26] for the groups attached to the sulfur, the three points lie on a straight line (see Table V). The σ_I values would be expected to work for systems where conjugative effects are absent or small. The straight line that results for these three

donors indicates only a slight amount of conjugation of the sulfur with the phenyl ring in $C_6H_5SCH_3$. The iodine adduct of $CH_3C(O)SCH_3$, if the sulfur atom were the donor site, is predicted to have a heat of formation of -4.2 kcal. mole^{-1} from this relationship, whereas the measured heat of formation is -3.2 kcal. mole^{-1}. Since the carbonyl oxygen is the donor, the interaction with the sulfur would be appreciably smaller than 3.2 kcal. mole^{-1}, assuming no unusual entropy effects. This is taken as indicative of considerable C–S π-bonding in $CH_3C(O)SCH_3$. The presence of extensive π-bonding in this donor, but little in $C_6H_5SCH_3$, can be attributed to more effective C–S π-overlap in the former compound because of the contraction in the size of the sulfur orbitals that results from electron withdrawal by the acetyl group. This strong electron withdrawal from sulfur can be seen in the value 143 c.p.s. for $J_{C^{13}H}$ in the S-methyl group of $CH_3C(O)SCH_3$, a much larger coupling constant than for other types of S-methyl groups. It should also be noted that the S-methyl group in $CH_3SC(O)N(CH_3)_2$ experiences an electron withdrawal similar to that in $CH_3C(O)SCH_3$.

TABLE V

SUM OF σ_I VALUES[a] OF GROUPS ATTACHED TO SULFUR

	Sum of σ_I values	$-\Delta H$ toward I$_2$, kcal. mole^{-1}
$(C_2H_5)_2S$	-0.10	7.8
$C_6H_5SCH_3$	$+0.05$	6.1
$(C_2H_5S)_2$	$+0.20$	4.6
$CH_3C(O)SCH_3$	$+0.23$	3.2

[a] See ref. 25.

The absence of a barrier to rotation at room temperature in the compound $CH_3SC(O)N(CH_3)_2$ has been interpreted as indicating extensive C–S π-bonding in the $RSC(O)R'$ system. In spite of extensive carbon-sulfur π-bonding, the carbonyl oxygen is not so strong a donor in $CH_3C(O)SCH_3$ as in $CH_3C(O)N(CH_3)_2$. This is attributed to greater electron withdrawal through the σ-system by the $-S-CH_3$ group than by the $-N(CH_3)_2$ group. This is supported by the σ_I values of $+0.25$ and $+0.10$ for the S–CH$_3$ and –N(CH$_3$)$_2$ groups, respectively.[25]

It is found that $CH_3C(S)N(CH_3)_2$ is a much stronger donor (as indicated by the enthalpy of adduct formation) toward iodine than is $CH_3CON(CH_3)_2$, while the donors have nearly equal strength toward phenol. This behavior is similar to that of the other sulfur and analogous oxygen donors listed in Table II. The smaller, more electronically compact oxygen interacts more strongly with hydrogen bonding or polar acids, whereas the more easily distorted sulfur interacts more strongly with the more easily distorted acid iodine.

(22) H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Japan*, **33**, 1660 (1960).

(23) (a) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 1471 (1959); (b) N. Muller, *ibid.*, **36**, 359 (1962); (c) H. Dreeskamp and E. Sackmann, *Z. physik. Chem.* (Frankfurt), **34**, 273 (1962).

(24) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **41**, 2642 (1963).

(25) R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958).

(26) NOTE ADDED IN PROOF.—Recently the σ_I value for RS$^-$ was reported to be $+0.19$ [R. W. Taft quoted by P. Wells, *Chem. Rev.*, **63**, 171 (1963)] instead of $+0.25$.[25] The point for $CH_3C(O)SCH_3$ falls below the line drawn through these points. The reason for this change is not presented.