5.80 and 6.06 μ, indicative of the ester carbonyl and carbon–carbon double bond, respectively.

Anal. Calcd for $C_9H_{14}ClNO_2$: C, 53.07; H, 6.93; Cl, 17.41; N, 6.88. Found: C, 53.34; H, 6.98; Cl, 16.96; N, 7.10.

B. Less Than 0.1 Mole of Sodium Ethoxide.—Evaporation of the ethanol (filtering periodically) and distillation of the residual oil produced, following a small forerun of II, ethyl N-carbethoxy-ϵ-aminocaproate (IV), bp 132.5–134° (0.2 mm), $n^{24}D$ 1.4446.

Anal. Calcd for $C_{11}H_{21}NO_4$: C, 57.12; H, 9.15; N, 6.06. Found: C, 57.17; H, 9.13; N, 6.08.

During the reflux period, placement of a cold trap after the water condenser allowed for the recovery of ethyl chloride, identified by boiling point and infrared spectrum. Furthermore, when IV was synthesized by an alternate method,[6] its boiling point and infrared spectrum were identical with that of our material.

Acid Solvolysis of 1-Chlorocarbonyl-2-chloro-4,5,6,7-tetrahydro-1H-azepine (I).—Compound I (9.7 g) was dissolved in 50 ml of ethanolic hydrogen chloride and the solution was stirred and refluxed for 24 hr. Chromatography indicated 1.4% I, 13.25% II, and 85.35% IV.

Basic Solvolysis of 1-Carbethoxy-2-chloro-4,5,6,7-tetrahydro-1H-azepine (II).—Compound II (12.5 g 0.0615 mole) was added to a solution of 1.4 g (0.0615 g-atom) of sodium dissolved in 75 ml of anhydrous ethanol and the mixture was stirred and refluxed for 24 hr. After filtration and evaporation of the ethanol, 4.3 g of II and 3.3 g of III were recovered by fractional distillation. Mixtures of II and III were similarly produced when the molar ratio of sodium ethoxide to II was decreased to 0.5 and 0.2.

Acid Solvolysis of 1-Carbethoxy-2-chloro-4,5,6,7-tetrahydro-1H-azepine (II).—Three milliliters of II was added to 25 ml of anhydrous ethanol containing dissolved hydrogen chloride and the solution was stirred and refluxed for 24 hr. Chromatography indicated 58.8% II and 41.2% IV.

Acknowledgment.—The author is grateful to Mr. J. Frank for the chromatographic separations and to Drs. M. Litt and H. K. Reimschuessel for their encouragement and suggestions.

Charge Distribution, Electric Moments, and Molecular Structure of Thiols and Thio Ethers

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Received May 19, 1966

It is known that divalent sulfur, because of its lone pair, is capable of releasing electrons in conjugative interactions with electron-deficient groups or with electron-withdrawing unsaturated groups through their mesomeric ability.[1] It has also been shown that the sulfur atom in sulfides can expand its valence shell to a decet.[2] In this paper, using the method of Smith, *et al.*,[3] the dipole moments of thiols and thio ethers have been calculated and compared with the experimental ones. The difference in moments have been explained on the basis of the above ideas.

Calculation

In this method each bond is uniquely characterized by two parameters, but the effective moment of each depends on the whole molecule. One of the parameters (β) is derived from bond polarizabilities (Table I). The other parameter (γ) must be obtained from dipole moment data. Bond angles and bond distances are taken from Sutton's table of interatomic distances.[4] The results of the calculations are summarized in Tables II–IV.

TABLE I

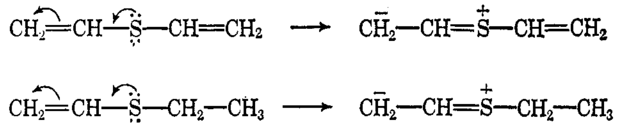
PARAMETERS USED IN CALCULATING THE CHARGE DISTRIBUTION

Bond (a—b)	β_{ab}	γ_{ab}	Basic molecule	Moment used[a] to derive γ_{ab}, D.
H—C	0.13	0.00	...	...
H—S	0.083	0.736	Hydrogen sulfide	1.17
Cl—C	0.71	−1.490	Methyl chloride	1.85
S—C	β_s^c = 0.459			
		$\alpha_{C'-S}$ = 1.560	Dimethyl sulfide	1.45
	β_c^s = 0.832			
C—C	β_c^c = 0.718	α_{cc} = 0	...	...
C=C	β_c^c = 1.70	α_{cc} = 0	...	...
C≡C	β_c^c = 2.84	α_{cc} = 0	...	...

[a] A. L. McClellan, "Table of Experimental Dipole Moments," W. H. Freeman and Co., London, 1963.

Discussion

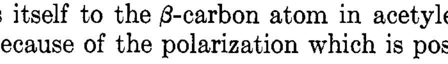
The close agreement between calculated and observed values (Table IV) for saturated thiols and thio ethers show that effects other than induction are absent. However, the observed low moments of divinyl sulfide and vinyl ethyl sulfide are due to conjugation between the unsaturated group and the lone pair (nonbonding) p electrons on the sulfur atom, leading to polar resonance structures. The negative differences in the moment of divinyl ether and ethoxypropyne show that such structures are more predominant in oxygen than in sulfur compounds. This concept of electron-pair release, involving a contribution from 2p-3p π bond, is supported by the data on the effect of the sulfide group on chemical reactivity,[5] bond distances,[1] and spectra.[6]



$$CH_2{=}CH{-}\ddot{S}{-}CH{=}CH_2 \longrightarrow \overset{-}{C}H_2{-}CH{=}\overset{+}{S}{-}CH{=}CH_2$$

$$CH_2{=}CH{-}\ddot{S}{-}CH_2{-}CH_3 \longrightarrow \overset{-}{C}H_2{-}CH{=}\overset{+}{S}{-}CH_2{-}CH_3$$

It has been proved[7,8] that the nucleophilic group attaches itself to the β-carbon atom in acetylenic thio ethers because of the polarization which is possible for



$$HC{\equiv}C{-}S{-}Et \longrightarrow \overset{+}{C}H{=}C{=}\overset{-}{S}{-}Et$$

an atom belonging to the second period of the periodic system. The positive difference between the observed and the calculated moments for acetylenic thio ethers, is due to contributions from such structures as given above. The sp carbon atom because of its higher

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

(2) G. Cilento, *Chem. Rev.*, **60**, 147 (1960).

(3) R. P. Smith, T. Ree, J. L. Magee, and H. Eyring, *J. Am. Chem. Soc.*, **73**, 2263 (1951).

(4) L. E. Sutton, Tables of Interatomic Distances and Configuration in Molecules and Ions, Special Publication No. 11, The Chemical Society, London, 1958.

(5) F. G. Bordwell, G. D. Cooper, and H. Morita, *J. Am. Chem. Soc.*, **79**, 376 (1957).

(6) C. E. Scott and C. C. Price, *ibid.*, **81**, 2672 (1959).

(7) H. C. Volger and J. F. Arens, *Rec. Trav. Chim.*, **77**, 1170 (1958).

(8) H. J. Boonstra, L. Brandsma, A. M. Wiegman, and J. F. Arens, *ibid.*, **78**, 252 (1959).

TABLE II

FORMAL CHARGE DISTRIBUTION IN THIOLS

Molecule	C_1	C_2	H_1	H_2	S	H attached to S
H_2S	...	...	...	...	−1.263	+0.632
MeSH	+0.444	...	+0.058	...	−1.249	+0.633
EtSH	+0.378	+0.128	+0.049	+0.017	−1.285	+0.630
i-PrSH	+0.329	+0.112	+0.043	+0.014	−1.311	+0.627
t-BuSH	+0.290	+0.098	...	+0.013	−1.347	+0.647

TABLE III

FORMAL CHARGE DISTRIBUTION IN THIO ETHERS

	Molecule	C_1	C_2	C_3	C_4	C_5	H_1	H_2	H_3	H_4	H_5	S	Cl
1.	Me_2S	+0.446	...	...	...	...	+0.058	...	...	...	...	−1.240	...
2.	Et_2S	+0.375	+0.128	...	...	...	+0.049	+0.017	...	...	...	−1.302	...
3.	*i*-Pr_2S	+0.324	+0.110	...	...	...	+0.042	+0.014	...	...	...	−1.345	...
4.	*t*-Bu_2S	+0.285	+0.097	...	...	...	...	+0.013	...	...	...	−1.378	...
5.	$(ClCH_2\cdot CH_2—)_2S$	+0.815	+0.772	...	...	...	+0.106	+0.100	...	...	...	−0.921	−0.942
6.	$(CH_2{=}CH—)_2S$	+0.356	+0.202	...	...	...	+0.046	+0.027	...	...	...	−1.319	...
7.	$(CH_2{=}CH—)S—Et$	+0.356	+0.204	+0.376	+0.128	...	+0.046	+0.026	+0.049	+0.017	...	−1.311	...
8.	$HC{\equiv}C\text{-}S\text{-}Et$	+0.364	+0.259	+0.374	+0.129	...	...	+0.034	+0.049	+0.016	...	−1.307	...
9.	$(Me—C{\equiv}C—)_2S$	+0.339	+0.223	+0.076	...	...	...	...	+0.010	...	...	−1.334	...
10.	$(Et—C{\equiv}C—)_2S$	+0.336	+0.221	+0.065	+0.022	...	...	...	+0.008	+0.003	...	−1.337	...
11.	$Me—C{\equiv}C—S—Et$	+0.340	+0.224	+0.076	+0.374	+0.127	...	...	+0.010	+0.049	+0.016	−1.317	...
12.	SCl_2	...	...	...	...	...	...	...	...	...	...	+0.460	−0.230
13.	$Cl_3C—S—Cl$	+1.532	...	...	...	...	...	...	...	...	...	+0.084	−0.427 (S) −0.403 (C)

TABLE IV

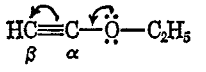
CALCULATED AND OBSERVED ELECTRIC MOMENTS OF THIOLS AND THIO ETHERS

		Dipole moment, D.			
	Molecule	Calcd	Obsd	Difference	Ref
1.	H_2S	...	1.17	...	*a*
2.	MeSH	1.34	1.26	−0.08	
3.	EtSH	1.35	1.39	+0.04	
4.	*i*-PrSH	1.42	1.53	+0.11	
5.	*t*-BuSH	1.43	1.55	+0.12	
6.	Me_2S	...	1.45	...	
7.	Et_2S	1.44	1.61	+0.17	*b*
8.	*i*-Pr_2S	1.57	1.67	+0.10	
9.	*t*-Bu_2S	1.55	1.57	+0.02	
10.	$(ClCH_2\cdot CH_2)_2S$	2.26	1.76	−0.50	*a*
11.	$(CH_2{=}CH—)_2S$	1.47	1.20	−0.27	
12.	$(CH_2{=}CH—)—S—Et$	1.46	1.36	−0.10	*c*
13.	$HC{\equiv}C—S—Et$	1.47	1.67	+0.20	
14.	$Me\cdot C{\equiv}C—S—Et$	1.47	1.61	+0.14	
15.	$(Me\cdot C{\equiv}C—)_2S$	1.49	1.68	+0.19	
16.	$(Et\cdot C{\equiv}C—)_2S$	1.48	1.66	+0.18	
17.	SCl_2	...	0.56	...	*a*
18.	$Cl_3C\cdot S\cdot Cl$	0.84	0.56	−0.28	
19.	$(CH_2{=}CH)_2O$	1.28	1.06	−0.22	*d*
20.	$Me\cdot C{\equiv}C—O—Et$	1.46	1.29	−0.17	

[a] See Table I, footnote *a*. [b] C. W. N. Cumper, J. F. Read, and A. I. Vogel, *J. Chem. Soc.*, 5323 (1965). [c] W. Drenth, G. L. Hekkert, and B. G. Zwanenburg, *Rec. Trav. Chim.*, **81**, 313 (1962). [d] S. K. Ramalingam and S. Soundararajan, unpublished results.

electronegativity[9] compared to sp^2 carbon atom, contracts the d orbitals of sulfur, when an overlap between the contracted d orbital and p orbital takes place leading to a double bond between carbon and sulfur.

On the other hand, the only possible polarization for acetylenic ethers is



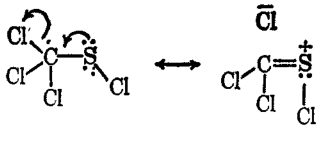
$$\underset{\beta}{HC}\equiv\underset{\alpha}{C}—\ddot{O}—C_2H_5$$

which explains why nucleophilic groups always react with the α-carbon atom and electrophilic groups with β-carbon atom. This is confirmed by the negative difference in moment obtained for ethoxypropyne. In agreement with this are the dipole moment calculations of Drenth, *et al.*,[10] who have estimated the amount of charge shift in ethoxyethyne and ethylthioethyne to be 0.11 and 0.06 e, respectively for the resonance structure

$$\overset{\delta-}{—C}\equiv C—\overset{\delta+}{X}—$$

where X is oxygen or sulfur.

It has been shown recently by Williams[11] that the high negative potentials of lone pairs are decreased by delocalization toward nearby nuclei. The low observed moment in trichloromethanesulfenyl chloride is due to the stabilization of the antibonding orbitals at the carbon atom by electron withdrawal from sulfur owing to increased effective nuclear charge on carbon. The reactive lone pair on sulfur then overlaps with the electron-deficient antibonding orbital of carbon with the result the that observed moment is less than the calculated moment. In valence bonds terms this can be represented as



In the case of β,β'-dichlorodiethyl sulfide the possibility of rotation of groups precludes any assessment of the moment.

Acknowledgment.—The authors thank Professor M. R. A. Rao for his keen interest and encouragement, and one of them (V. N. K.) thanks the Council of Scientific and Industrial Research (India) for a fellowship.

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[9] H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

[10] See Table IV, footnote *c*.

[11] J. Williams, *Trans. Faraday Soc.*, **57**, 2087 (1961).