of the CF_3 group to phosphorus (${}^2J_{PF}$ = 108 Hz) and from unresolved coupling to 18 equivalent protons of the three $N(CH_3)_2$ groups yielding an overall peak width consonant with the value of ${}^5J_{FH}$ obtained from the ${}^1H$ spectrum. The ${}^{31}P$ NMR spectrum is a quartet of multiplets of 19 lines due to coupling of the phosphorus to three equivalent fluorine atoms (${}^2J_{PF}$ = 107.5 Hz) and the 18 equivalent protons of threee $N(CH_3)_2$ groups (${}^3J_{PH}$ = 10.3 Hz). The ${}^{31}P$ chemical shift (δ vs. P_4O_6: +69 ppm) is in the correct range for a phosphonium salt[16] and is comparable to the ${}^{31}P$ chemical shifts of $CH_3P[N(CH_3)_2]_2F^+$ (+40.6 ppm) and $C_6H_5P(F)[N(CH_3)_2]_2^+$ (+56.0 ppm).[17] All of the ${}^{31}P$ chemical shifts are much smaller than those expected[16,18] for analogous phosphoranes.

Alkaline hydrolysis of $CF_3P[N(CH_3)_2]_3^+PF_6^-$ yields (eq 5) 1 molar equiv of CF_3H and transforms the cation to

$$(CF_3)P[N(CH_3)_2]_3^+ + H_2O \rightarrow CF_3H + OP[N(CH_3)_2]_3 + H^+ \qquad (5)$$

$OP[N(CH_3)_2]_3$. The PF_6^- ion resists hydrolysis in alkaline solution.[16] Similar resistance of the P–N linkage to hydrolysis under similar conditions has been observed in some (trifluoromethyl)dimethylaminophosphoranes.[18]

Formation of the aminophosphonium salts from CF_3PCl_4 and $(CF_3)_2PCl_3$ rather than the phosphoranes may be due to the prohibitive steric requirements of the $(CH_3)_2N$ group as well as the tendency of the system to form Cl^-. The successful synthesis of six-coordinate catechol phosphates[19] suggests that steric restrictions are probably unimportant relative to electronic factors. Further study of the system would likely be rewarding.

Acknowledgment. We thank the National Research Council of Canada for financial support of this work and Dr. K. I. The for some experimental assistance.

Registry No. $CF_3P[N(CH_3)_2]_3Cl$, 60439-31-8; $(CH_3)_2NH_2Cl$, 506-59-2; CF_3H, 75-46-7; $(CF_3)_2PCl_2[N(CH_3)_2]$, 60478-97-9; $CF_3P[N(CH_3)_2]_3^+PF_6^-$, 60439-33-0; $(CF_3)_2PCl_3$, 353-77-5; $(CH_3)_2NH$, 124-40-3; CF_3PCl_4, 1066-48-4; ${}^{31}P$, 7723-14-0; $CF_3P[N(CH_3)_2]_3^+Cl^-$, 60439-34-1.

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Trends in the Charge Distribution in Sulfanes, Sulfanesulfonic Acids, Sulfanedisulfonic Acids, and Sulfurous Acid

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Trends in the charge distribution of sulfur chains belonging to the families H_2S_x, HS_xSO_3H, $S_x(SO_3H)_2$, and H_2SO_3 were calculated with an extended Hückel model based on spectral atomic parameters. The results were correlated to the acidity constants of sulfanes, data on the reaction mechanism of sulfur degradation by sulfite, and the formation of elemental sulfur from thiosulfate. Furthermore, the relative stability of various sulfite species was considered. The charge trends in sulfanes parallel the trend of the experimentally determined acid constants. The charge distribution in the SO_3^- family correlated well to the observed stability of these species, and the charge distribution in sulfanemonosulfonic acids supports a model based on experimental study of the degradation of labeled sulfur by sulfite.

Introduction

The main purpose of the present work was to determine the qualitative trends of the charge distribution in families of unsubstituted and substituted catenated sulfur species and to test whether the charge distributions calculated for the free molecules could be correlated to the experimentally established behavior of the aqueous species. These species are all related to Wackenroder's liquid, which is obtained by the reaction of H_2S with SO_2. The reactions in this system are important intermediates in many SO_2-abatement reactions which are still very poorly understood.

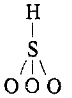
Several semiempirical models have been successfully used to compute the properties of various inorganic sulfur molecules. Miller and Cusachs[2,3] calculated the electronic energy levels of S_4, S_6, and S_8 rings and H_2S, H_2S_2, and S_6^{2-} chains in order to determine the role of the sulfur 3d orbitals and to explain the stability of various molecules and their mixture in liquid sulfur. Buttet[4] used the Wolfsberg–Helmholtz method[5] to predict the diradical properties of S_4, S_6, S_8, and S_{10} chains. Müller and Heegn[6] used a three-dimensional free-electron model to predict the relative stability of elemental sulfur chains and rings. The properties of sulfanes and substituted sulfanes were computed and discussed by Feher,[7] who used Kuhn's electron gas model, McGlynn,[8] Boyd,[9] Seel,[10] Colton,[11] and Leibovici.[12] The electronic structure of S_8 has recently been reexamined by Palma[13] and Kortela.[14] Carlson and Pederson[15] conducted an ab initio calculation. Cotton[16] used the SCF–SW–X_2 method to study S_2^-, S_3^-, and S_3^{2-}. All calculations, including our own,[17] agree with Miller and Cusachs' finding[2,3] that the sulfur 3d orbitals have little effect on filler molecular orbitals, i.e., on ground-state properties, but influence unoccupied orbitals and the properties of excited states. In our previous work,[17] we calculated the energy of the first allowed electronic transition in H_2S_x ($2 \le x \le 8$), in the neutral diradical chains S_x ($2 \le x \le 8$), and in various rings and isomers of S_4, and in recent calculations[18,19] of S_x^-, S_x^{2-}, S_x^+, and S_x^{2+}, we found that our extended Hückel model, despite its simplified assumptions and many theoretical shortcomings, gave trends for transition energies of catenated sulfur species which were fully consistent with experimental observations and allowed interpretation and assignment of formerly unidentified species.

In the present paper three families of molecules have been chosen to test the value of such calculations for predicting chemical facts. First, we computed the trend of the charge on the last sulfur atoms in sulfanes to correlate it to the acid dissociation constant which has been measured by Schwarzenbach.[20]

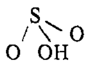
Second, we calculated the charge distribution in some members of the sulfanemonosulfonic acid series to determine trends as a function of chain length, dissociation, and location of the proton in the partly dissociated species, in order to predict the possible points of attack for nucleophilic reagents and the relative stability of the molecules.

It is now generally accepted that the formation[21] and degradation[22-24] of catenated sulfur in polar solvents involve nucleophilic reactions of $^-S_xSO_3H$, sulfanemonosulfonic acids. Schmidt[23] prepared such compounds, as well as the sulfanedisulfonic acids, formerly called polythionic acids, and demonstrated their close relationship with polysulfides and sulfanes. He deduced from his extensive observation an admittedly speculative model,[23] which is in conflict with the mechanisms proposed by Foss[24] and Wagner and Davis.[25]

Finally, we were interested in examining the charge distribution and the stability of some members of the sulfurous acid system, because sulfite and bisulfite are important reagents in many of the above-mentioned reactions. Furthermore, Raman and IR spectra of $MHSO_3$ and $MDSO_3$ show that the bisulfite ion exists in crystals and in aqueous solutions in the form **1a**. The species **1b** has not yet been conclusively observed.[26-30] We were curious to see whether the extended Hückel model, even though it is not specially suitable for small molecules, would indicate any charge distribution trends which might give us hints for the stability of the various species.



1a



1b

The Extended Hückel Method

As in our previous study,[17] our calculations follow the Wolfsberg–Helmholtz method described by Zerner and Gouterman.[31,32] The off-diagonal elements, H_{ij}, of the secular determinant have the form of eq 1. The interaction constant,[17,33] k, was set at 1.89. S_{ij} is the basis set overlap. The Coulomb integrals, H_{ii}, were evaluated as valence orbital ionization energies. The extended Hückel parameters for sulfur, hydrogen, and oxygen are the same as those used in our previous report.[17,18] The valence orbital ionization energies, α, are based on the observed spectroscopic data.[34] The 3d orbitals of sulfur were included in all calculations. The calculations involved an iterative procedure around atomic charge self-consistency. Zerner[35] pointed out that this procedure can lead to smoothing of the calculated atomic charge distributions. We used a computer program written by Davidson.[17]

$$H_{ij} = {}^1/_2 S_{ij}(H_{ii} + H_{jj})(k + \delta_{ij}(1 - k)) \qquad (1)$$

Molecular Geometries

Reliable structural data are available for only a few of the molecules treated in this work. The polysulfides consist of unbranched chains.[36-39] In order to simplify calculations, the molecular geometries of compounds of known structures were idealized wherever possible. For example, the species S_x^{2-} and HS_x^- were treated as zigzag planar chains, with S–S = 0.204 nm, S–H = 0.135 nm, and the bond angles SSS = 105° and HSS = 95°, rather than as helices or other three-dimensional structures, because our earlier work[17] had shown that this approximation gave data well within the limit of accuracy of our extended Hückel model. As our calculations are not very sensitive toward small changes in bond length, we chose an appropriate, representative bond length and did not calculate for each molecule all of the different values observed for different compounds. The sulfanemono- and -disulfonates and their corresponding acids consist of sulfur chains terminated by one or two sulfonate or hydrogen sulfonate groups. The bond distances[40-43] are $S–SO_3$ = 0.212 nm, S–O = 0.144 nm, S–(OH) = 0.155 nm, and O–H = 0.098 nm. An exception is monosulfide monosulfonate, thiosulfate, for which $S–SO_3$ is 0.200 nm.[44] The bond angles are SSO = 109°, SOH = 104°, and OSO = 110°. The structures of the sulfurous acid species were modeled after the x-ray structure of Na_2SO_3.[45] The bond parameters are S–O = 0.150 nm, S–(OH) = 0.160 nm, S–H = 0.135 nm, and O–H = 0.098 nm, with bond angles of OSO = 109°, HSO = 110°, and SOH = 104°. The sulfite and bisulfite ions have pyramidal C_{3v} symmetry, while $(HO)SO_2^-$ and the two sulfurous acids were given C_s symmetries.

(1) Sulfanes and Sulfide Ions. The results of our calculations on charge densities of sulfanes[17] and hydrogen polysulfides are listed in Table I. The charge distribution in dinegative sulfides, discussed above, is also included in Table I. The data indicate that the atoms in sulfanes are almost neutral and the charges on the central and terminal sulfur atoms are essentially constant and independent of chain length. This charge distribution corresponds to what one would expect for a molecule with a localized full octet on all molecules of the chain. The charge is far more evenly distributed than even in the neutral diradical elemental sulfur chains,[17-19] and our calculations indicate that sulfanes are nonpolar molecules. This corresponds to the fact that they dissolve readily in nonpolar solvents. Our model is too crude to establish a significant trend for charge distribution at the hydrogen atom which might correlate to the trend in the observed NMR spectra.[46] The hydrogen atoms of the sulfanes in Table I carry a small negative charge; if d orbitals are omitted in the calculation,[17] the hydrogens are neutral or carry a small positive charge.

The hydrogen polysulfide ions HS_x^- carry two different terminal functions. Table I shows that in long molecules the sulfane end has a charge distribution similar to that of the sulfanes, and likewise, the sulfide part of the molecule has a charge distribution analogous to that in dinegative sulfide ions. In all molecules the negative charge increases from the sulfane end toward the terminal sulfur atom on the sulfide end. In molecules with five or fewer sulfur atoms, the charge distribution of both functional groups differs significantly from that in sulfanes and disulfides: the sulfide end in HS_5^- and HS_4^- has the same charge distribution as in large molecules, because the sulfide charge can be partly absorbed by the neutral sulfane part of the chain, while in the disulfide ions, the charges of the identical end groups block charge transfer beyond the middle of the chain. In HS_4^- and shorter molecules, the sulfide charge significantly affects the charge distribution between hydrogen and the last sulfur atom at the

Table I. Calculated Charges and Dissociation Constants of Sulfanes

Chain length	Atom	Charge			Dissocn const[a]	
		H_2S_x	HS_x^-	S_x^{2-}	pK_1	pK_2
2	H	−0.036	−0.143			9.7
	S	0.036	−0.345			
	S	0.036	−0.512			
	H	−0.036			5.0	
3	H	−0.046	−0.093			7.5
	S	0.028	−0.161	−0.697		
	S	0.036	−0.263	−0.607		
	S	0.028	−0.480	−0.697		
	H	−0.046			4.2	
4	H	−0.049	−0.076			6.3
	S	0.021	−0.077	−0.589		
	S	0.029	−0.124	−0.422		
	S	0.029	−0.255	−0.422		
	S	0.021	−0.469	−0.589		
	H	−0.049			3.8	
5	H	−0.052	−0.065			5.7
	S	0.016	−0.035	−0.516		
	S	0.024	−0.056	−0.346		
	S	0.025	−0.136	−0.277		
	S	0.024	−0.252	−0.346		
	S	0.016	−0.456	−0.516		
	H	−0.052			3.5	
6	H	−0.070	−0.053			(~5.2)
	S	0.015	−0.020	−0.495		
	S	0.026	−0.021	−0.300		
	S	0.029	−0.068	−0.205		
	S	0.029	−0.120	−0.205		
	S	0.026	−0.252	−0.300		
	S	0.015	−0.466	−0.495		
	H	−0.070			(~3.2)	
7	H	−0.055	−0.056			(~4.8)
	S	0.010	−0.006	−0.481		
	S	0.017	−0.002	−0.280		
	S	0.018	−0.027	−0.170		
	S	0.019	−0.062	−0.137		
	S	0.018	−0.138	−0.170		
	S	0.017	−0.255	−0.280		
	S	0.010	−0.455	−0.481		
	H	−0.055			(~3)	
8	H	−0.026	−0.044			(~4.4)
	S	0.008	−0.004	−0.472		
	S	0.008	0.005	−0.270		
	S	0.006	−0.009	−0.153		
	S	0.004	−0.038	−0.105		
	S	0.004	−0.071	−0.105		
	S	0.006	−0.130	−0.153		
	S	0.008	−0.252	−0.270		
	S	0.008	−0.458	−0.472		
	H	−0.026			(~2.9)	

[a] From ref 20.

sulfane end. Figure 1 shows the calculated charge of the terminal sulfur atom of the HS_x^- and the S_x^{2-} series as a function of chain length. Both curves converge toward a charge value of about 0.46 for long chains. The kink of the HS_x^- curve at $x = 3$ and of S_3^{2-} at $x = 6$ shows that most of the charge of the sulfide group is confined to three neighbor atoms. If our calculations are significant, one would expect that the chemical properties of sulfanes and sulfide chains would show trends similar to those in Figure 1. There are no experimental studies of the free molecules which can be used to test our model. However, the reactivity of sulfanes has been established in aqueous solution. Figure 2 shows the dissociation constants pK_1 and pK_2 measured by Schwarzenbach and Fischer,[20] as well as the charge which we computed for the terminal sulfur atom in the corresponding species. Figure 2 also shows $pK_2 - pK_1$, i.e., ΔpK for each sulfane pair, and the charge difference of the terminal sulfur atoms of the HS_x^- and

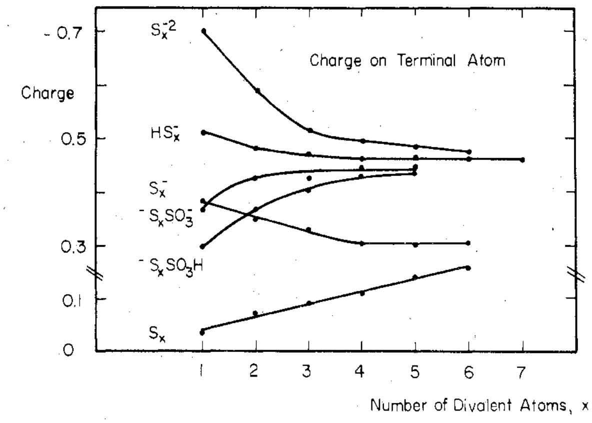


Figure 1. Charge on terminal atom of polysulfide species.

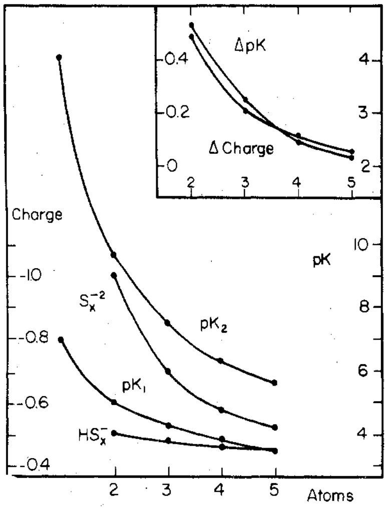


Figure 2. Charge on terminal atom and dissociation constant of sulfanes.

S_x^{2-} species vs. chain length. The similarity of the trends shows that our crude extended Hückel model of free molecules gives qualitatively correct charge distribution trends for aquated species. The figure also suggests that charge distribution is more strongly correlated to dissociation constants than inorganic chemists normally consider.

Our calculations also yield energy levels of all of the above species. The correlation between color, electronic spectra, and transition energy of sulfanes has previously been discussed.[17] The trends of transition energies of HS_x^- suggest that small homologues should be colorless and that long chains should absorb in the visible spectrum and appear yellow, as is indeed observed.[19]

(2) Sulfanemono- and -disulfonic Acid Systems. Tables II and III list the calculated charges on atoms of the mono- and disulfonic acid systems. Only unique atoms are shown. For the disulfonic acid group values for only the free acids and their dinegative anions are shown. For monosulfonic acids both monoprotonated anions $HS_xSO_3^-$ and $^-S_xSO_3H$ are also included. In all species, the sulfonate atom is the most positively charged atom; its nearest neighbor is the second most charged atom, and the charge changes smoothly on further adjoining sulfur atoms. Likewise, in the two series of molecules with sulfur at the chain terminal, the negative charge decreases from the terminal to the penultimate sulfur, etc. Figure 1 shows the charge of the chain ends for $S_xSO_3^{2-}$ and $^-S_xSO_3H$ groups vs. chain length. For long chains, the curves converge to a charge of about 0.45, i.e., the value of sulfide tails of long S_x^{2-} and HS_x^-. The curves show that in chains with five or fewer sulfur atoms, charge from the sulfide end of the chain

Table II. Calculated Charges in Sulfanemonosulfonic Acids and Their Ions

Species	Atom	HS_xSO_3H	$HS_xSO_3^-$	$^-S_xSO_3H$	$^-S_xSO_3^-$
$H_2S_2O_3$	H	0.133	0.072		
	S	0.189	0.132	−0.167	−0.244
	S	0.405	0.290	0.258	0.127
	O^a	−0.401	−0.496	−0.514	−0.628
	O	−0.244	−0.502	−0.312	−0.628
	H	0.318		0.252	
$H_2S_3O_3$	H	0.045	0.006		
	S	0.122	0.079	−0.295	−0.365
	S	0.193	0.110	−0.012	−0.114
	S	0.387	0.279	0.297	0.175
	O^a	−0.406	−0.491	−0.480	−0.567
	O	−0.243	−0.491	−0.295	−0.562
	H	0.308		0.265	
$H_2S_4O_3$	H	0.000	−0.018		
	S	0.090	0.060	−0.367	−0.422
	S	0.127	0.088	−0.106	−0.174
	S	0.182	0.124	0.067	0.011
	S	0.382	0.267	0.325	0.216
	O^a	−0.418	−0.510	−0.458	−0.544
	O	−0.246	−0.502	−0.276	−0.542
	H	0.302		0.273	
$H_2S_5O_3$	H	−0.013	−0.023		
	S	0.067	0.042	−0.403	−0.415
	S	0.080	0.050	−0.167	−0.213
	S	0.108	0.064	0.017	−0.056
	S	0.170	0.102	0.112	0.054
	S	0.376	0.267	0.337	0.230
	O^a	−0.420	−0.504	−0.453	−0.535
	O	−0.249	−0.496	−0.272	−0.529
	H	0.301		0.282	
$H_2S_6O_3$	H	−0.025	−0.031		
	S	0.030	0.018	−0.423	−0.446
	S	0.052	0.034	−0.209	−0.234
	S	0.076	0.050	−0.042	−0.088
	S	0.116	0.080	0.047	0.016
	S	0.175	0.121	0.124	0.078
	S	0.375	0.261	0.352	0.243
	O^a	−0.423	−0.514	−0.437	−0.525
	O	−0.250	−0.503	−0.260	−0.518
	H	0.297		0.285	
$H_2S_7O_3$	H	−0.031	−0.038		
	S	0.023	0.029	−0.436	−0.441
	S	0.043	0.028	−0.228	−0.241
	S	0.058	0.025	−0.075	−0.106
	S	0.069	0.038	0.010	−0.021
	S	0.095	0.064	0.070	0.028
	S	0.162	0.106	0.140	0.093
	S	0.374	0.264	0.352	0.239
	O^a	−0.421	−0.507	−0.434	−0.517
	O	−0.250	−0.501	−0.255	−0.517
	H	0.298		0.291	

[a] Each molecule contains two oxygen of this type.

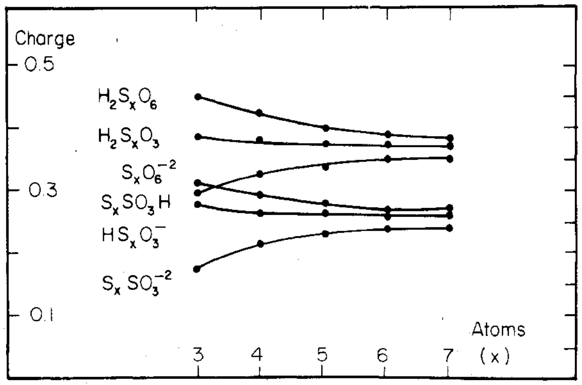


Figure 3. Charge on sulfonate atom in compounds containing catenated sulfur.

Table III. Calculated Charges of Unique Atoms in Sulfanedisulfonic Acid and Its Ions

Molecule	Atom	$H_2S_xO_6$	$S_xO_6^{2-}$
$H_2S_3O_6$	H	0.334	
	O	−0.219	−0.470
	O^a	−0.361	−0.470
	S	0.453	0.312
	S	0.308	0.197
$H_2S_4O_6$	H	0.318	
	O	−0.223	−0.478
	O^a	−0.385	−0.485
	S	0.423	0.294
	S	0.253	0.155
$H_2S_5O_6$	H	0.312	
	O	−0.235	−0.487
	O^a	−0.406	−0.502
	S	0.401	0.279
	S	0.230	0.145
	S	0.207	0.132
$H_2S_6O_6$	H	0.306	
	O	−0.241	−0.494
	O^a	−0.409	−0.497
	S	0.391	0.269
	S	0.197	0.125
	S	0.165	0.093
$H_2S_7O_6$	H	0.304	
	O	−0.246	−0.500
	O^a	−0.418	−0.506
	S	0.381	0.270
	S	0.189	0.128
	S	0.144	0.082
	S	0.129	0.062

[a] Each molecule contains two atoms of this type.

Table IV. Calculated Charges in Sulfurous Acid Isomers and Their Ions[a]

Parent acid	Atom	H_2SO_3	HSO_3^-	SO_3^{2-}
$HSO_2(OH)$	H	0.170	0.096	
	S	0.428	0.304	0.009
	O	−0.361	−0.467	−0.670
	O	−0.216	−0.467	−0.670
	H	0.341		
$(HO)_2SO$	S	0.316	0.163	0.009
	O	−0.416	−0.531	−0.670
	O	−0.256	−0.345	−0.670
	H	0.306	0.244	

[a] Relative stabilities: $HSO_3^- > (HO)SO_2^-$; $HSO_2(OH) > (HO)_2SO$.

is drawn into the sulfonate part of the molecules. Figure 3 illustrates how the charge on the sulfonate sulfur changes with chain length and the nature of the other functional group. The curves representing the six homologous series converge to two charge values: 0.29+ for sulfonate sulfur and 0.38+ for sulfonic acid sulfur. The difference, 0.11+, represents the influence of the proton on an adjoining oxygen upon the charge of the sulfonate sulfur. This difference is almost identical with that calculated for the corresponding free sulfurous acid species (Table IV). The influence of substituents on the sulfide chain also appears in Figure 3. The sulfonate group draws charge from the chain and thus increases the positive charge, and the sulfide acts as a donor and decreases the positive charge on the chain, while the neutral sulfane group exhibits a small acceptor effect. The functional group effect rapidly diminishes with increasing distance and has about the same interaction radius as observed above.

The molecular orbital energies of the sulfonic acid species show the same trend as all sulfur chain species. Thus, we expect long chains to have a yellow color. The calculated transition energies for $S_xO_6^{2-}$ and $H_2S_xO_6$ are only slightly lower than those computed from the ultraviolet spectra reported by Schmidt and Sand.[47] All species $S_xO_6^{2-}$, $H_2S_xO_6$, HS_xSO_3H, $^-S_xSO_3H$, $S_xSO_3^{2-}$, and $HS_xSO_3^-$ can be expected to be colorless or slightly light yellow.

(3) Sulfurous Acid System. The charge distribution in the

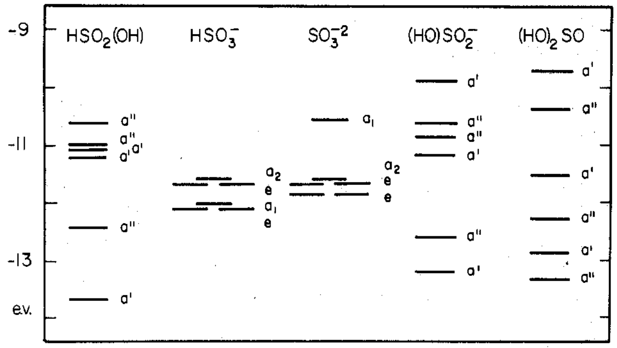


Figure 4. The six highest filled molecular orbitals of molecules of the sulfurous acid family.

five members of the sulfurous acid family is shown in Table IV. The best known members are the sulfite ion and the hydrogen sulfite, also called bisulfite. Free sulfurous acid has not yet been observed; instead, aquated SO_2, which is the sulfurous acid anhydride, exhibits the spectral and other properties of the free SO_2 molecules.[48] Aquated SO_2 can react with bisulfite to form $S_2O_5^{2-}$ which is called pyrosulfite, or more properly disulfite.[26,27] The species $HS_2O_5^-$ is not known. The disulfite species will not be further discussed in this paper.[49] A further peculiarity of this system is that IR and Raman spectra of aqueous solutions and salts indicate that the proton of the bisulfite species is attached to the sulfur[26-30] and not to an oxygen, as many text and reference books still claim. We decided to calculate molecular orbital energy levels and the charge distribution of a series of molecules of this family, even though the Hückel model is not specially suitable for predicting the properties of small molecules and despite the fact that the properties of small free ions might be quite different from those in aqueous solution. Figure 4 shows the six highest filled molecular orbitals of the five sulfurous acid family members. The energy levels of all ionic species are adjusted to fit the scale in order to facilitate comparison. The adjustment corresponds to the influence of a spherical stabilizing potential such as would be found in the presence of a polar solvent.

An analysis of the substituent atomic orbital coefficients of the molecular orbitals of SO_3^{2-}, Figure 4, reveals that both the e and the a_2 levels in C_{3v} symmetry represent nonbonding electron pairs localized on the oxygen atoms, while the a_1 level is an antibonding π^* orbital. If sulfite is protonated according to first-order electrostatics, the proton would choose the oxygen site and form $(HO)SO_2^-$. Figure 4 shows that this leads to a perturbation of the sulfite orbitals; in C_s symmetry the e levels are no longer degenerate and instead convert to a′ and a″ orbitals; the lowest energy a′ and a″ are no longer strictly nonbonding but are involved in the O–H bonding in $(HO)SO_2^-$; the sulfite a_2 orbital transforms as a″ of the bisulfite and the $a_1(\pi^*)$ as a′; the highest a′ orbital of bisulfite retains its S–O π^* character but only with respect to the two remaining terminating oxygens.

As stated above, all experiments show that the proton is bonded to the sulfur[26-30] of the sulfite. In this molecule the a_2 orbital and the highest three levels retain their character and their relative energy changes very little. However, the a_1 orbital loses its antibonding nature and becomes a combination oxygen nonbonding and S–H weakly bonding orbital, and its energy drops drastically. As a qualitative comparison of the six highest occupied MO's in Figure 4 suggests, HSO_3^- is more stable than $SO_2(OH)$: bond length[45,50] and S–O stretching frequency[51,52] considerations corroborate this finding. They show that the sulfite ion has some double-bond character. Thus, if a proton is bonded to an oxygen, the S–O bond order for one oxygen is reduced, and the energy gained by the O–H linkage is partly offset by the S–O weakening. The H–S bond, in contrast, strengthens the S–O bonds because electron density is "drawn out" of the S–O $\pi^*(a_1)$ orbital of the sulfite by the proton (Figure 4), as is demonstrated by the fact that the S–O stretching frequencies of HSO_3^- are significantly larger[26-30] than those reported for sulfite.[51] Thus, overall energy considerations favor the H–S bond in the bisulfite ion, even though O–H bonds are normally more stable than S–H.

The calculations for two geometries of fully protonated sulfurous acid, Figure 4, can be interpreted with the same arguments as for the bisulfite. Thus, we predict that sulfurous acid, in analogy with the lower oxy acids of phosphorus,[53] possesses a hydrogen–sulfur bond.

(4) Formation and Nucleophilic Degradation of Sulfur Chains. It is interesting to test whether the calculated charge distributions of the above molecules are in harmony with experimental chemical facts and to see whether our model supports reaction mechanisms proposed on the basis of different reasoning. We discuss here only three examples of reactions between species for which we have calculated charges: the acid-catalyzed decomposition of thiosulfate, the nucleophilic degradation of elemental sulfur, and the nucleophilic degradation of anionic polysulfides.

It is generally believed that eq 2–5, proposed by Davis,[21]

$$S_2O_3^{2-} + H^+ \rightarrow HSSO_3^- \qquad (2)$$

$$^-O_3SS^- + HS\text{-}SO_3^- \rightarrow HSSSO_3^- + SO_3^{2-} \xrightarrow[\text{fast}]{H^+} HSO_3^- \qquad (3)$$

$$^-O_3SS^- + HSS\text{-}SO_3^- \rightarrow HSSSSO_3^- + SO_3^{2-} \xrightarrow[\text{fast}]{H^+} HSO_3^-, \text{ etc.} \qquad (4)$$

$$\text{Until: } HS_{(n)}SO_3^- \rightarrow S_n + HSO_3^- \quad (n = 6, 8, 12) \qquad (5)$$

describe the formation of elemental sulfur from thiosulfate in concentrated hydrochloric acid. It is not immediately obvious why acids should react with thiosulfate to form sulfanemonosulfonic acid, because both sulfide and sulfite are Lewis bases. However, our calculations above confirm that $HS_xSO_3^-$ species are always more stable than $^-S_xSO_3H$. Thus, the proton attaches itself to the divalent sulfur, eq 2. Furthermore, our calculations predict that the nucleophile will always attack the sulfur atom adjoining the SO_3^- group, eq 3 and 4, because according to Table I it is the most positive atom of the sterically accessible atoms of the chain. This mechanism corresponds to that proposed by Schmidt,[23] who supported it by qualitative arguments aimed at supporting the experimental facts. The ring closure, eq 3, again, involves reaction between the atoms with the highest opposite charges. The reaction product does not depend on charge consideration but is influenced by the rate of chain formation which depends on concentration and temperature.

The explanations for the degradation of elemental sulfur by sulfite are more controversial.[54] The two most prominent mechanisms for thiosulfate formation from sulfite degradation of sulfur were proposed by Foss[55] and Schmidt.[23] They agree on the same initial and rate-determining step

$$S_8 + SO_3^{2-} \rightarrow {}^-S_8SO_3^- \qquad (6)$$

but differ on the remaining reaction path. Foss suggested

$$SO_3^{2-} + {}^-SSSSSSS\text{-}SSO_3^- \rightarrow {}^-SSSSSSSSO_3^- + S_2O_3^{2-} \qquad (7)$$

$$SO_3^{2-} + {}^-SSSSSS\text{-}SSO_3^- \rightarrow {}^-SSSSSSSO_3^- + S_2O_3^{2-}, \text{ etc.} \qquad (8)$$

and finally

$$SO_3^{2-} + {}^-S\text{-}SSO_3^- \rightarrow 2S_2O_3^{2-} \qquad (9)$$

Schmidt favored successive sulfite attack at the terminal sulfur atom

$$SO_3^{2-} + {}^-S\text{-}SSSSSSSSO_3^- \rightarrow {}^-SSSSSSSSO_3^- + S_2O_3^{2-}, \text{ etc.} \qquad (10)$$

until finally

$$SO_3^{2-} + {}^-S\text{-}SSO_3^- \rightarrow 2S_2O_3^{2-} \qquad (11)$$

Foss argued that thiosulfate was the most stable leaving group. Schmidt, for experimental reasons, argued that the reaction should involve the terminal sulfur atom of the sulfide group and postulated an elaborate charge delocalization scheme for the "lone pair" valence electrons[23] in order to explain why a nucleophile attacks preferentially what should be the most electron-rich sulfur atom. Contrary to Schmidt's delocalization hypothesis, our calculations, Table II, and Figure 2 show that a significant negative charge builds up on the terminal sulfur of the ${}^-S_xSO_3^-$ species. Thus, as in the preceding reaction, the sulfite and sulfide are unlikely to attack each other. However, in a basic environment the bisulfite is fully dissociated, and the positive charge of the sulfur atom in the sulfite group is exposed. Manne[56] computed a charge of 0.93+, we calculated a charge of 0.009+, Table IV, and other authors computed charges of 0.30+ and higher. Thus, the sulfide can attack the sulfonate atom in sulfite, and our calculations indicate that in a strong base the sulfide group, and not the sulfite, acts as the nucleophile. This model reconciles Foss' assumptions about the charge distribution in sulfanemonosulfonic acids and Schmidt's identification of the reactive groups without the need for Schmidt's unlikely charge delocalization scheme. The overall reaction involves transfer of a neutral sulfur atom.

The same consideration can be applied to the reactions of ionic polysulfides. Again there are two schools of thought with respect to the mechanisms involved. Wagner and Davis[25] argued that the preferred site of attack is on an internal sulfur which participates in the species' longest, therefore weakest, sulfur–sulfur bond, as determined by x-ray diffraction.[37] Schmidt,[23] again, cited experimental evidence, using ^{35}S, that a nucleophile will preferentially attack at the chain termini. He reported that $AsO_3H_2^-$ attacked 55% of S_3^{2-}, 89% of S_4^{2-}, and 94% of S_5^{2-} at the chain ends. If the nucleophile acts like thiosulfate, then one would expect the initial attack on the sulfide chain to be at the innermost atom, but if the nucleophile resembles sulfite, i.e., has a positive-charged thiophilic center, one would predict attack at the chain terminal. The nucleophile $AsO_3H_2^-$ conforms to our sulfitelike model. The observed trend in the relative preference of terminal sulfur among the three above sulfide ions corresponds exactly to what one would expect from our calculations, because the charge difference between central and terminal atoms, which is modest in S_3^{2-}, increases quickly with chain length. This gives substantial support to our model.

Summary and Conclusions

Our extended Hückel calculations confirm that the charge distribution within and among all families of neutral and charged elemental sulfur chains follow similar trends. The correlation between charge distribution and dissociation constants of sulfanes indicates that the extended Hückel model for free molecules yields data compatible with the behavior of real molecules, even in polar solvents. The calculated charge trends allow prediction of acid constants which are hard to measure. The calculations on sulfurous acid species are also compatible with experimentally confirmed facts, even though our extended Hückel model theoretically represents such small molecules poorly. It would be interesting to see whether better theoretical models for H_2SO_3 would give better quantitative results. Sulfanemonosulfonic acid, sulfanedisulfonic acid, and their ions are tailor-made for our model. The calculated charge distributions indicate a smooth transition from a negative sulfide tail to the positively charged sulfonate atom. The charge distribution predicts correctly the points of nucleophile attack, and comparison of charge distribution in sulfite and various families of reagents suggests a reaction mechanism which helps reconcile the conflicting models for nucleophile reactions involving sulfur chains and rings.

It would be valuable to calculate the charge distribution in very long chains to see at what chain length the charge on the terminal functional group converges. This might help to develop spectral and other analytical techniques to identify sulfur chains with more than 10 atoms, which occur in strongly basic aqueous sulfide solutions and probably in colloidal sulfur. Since our crude extended Hückel model,[32,33] developed for organic molecules, gives qualitatively correct charge distributions, relative stabilities, and electronic transition energies for many more molecules, belonging to diverse families of functional groups, without a single qualitatively incorrect prediction, it seems that these elemental sulfur species would make valuable models for calculation with more advanced methods.

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Registry No. H_2S_2, 13465-07-1; HS_2^-, 26693-74-3; H_2S_3, 13845-23-3; HS_3^-, 60789-08-4; S_3^{2-}, 60789-09-5; H_2S_4, 13845-25-5; HS_4^-, 60789-10-8; S_4^{2-}, 12597-07-8; H_2S_5, 13845-24-4; HS_5^-, 60789-11-9; S_5^{2-}, 60789-12-0; H_2S_6, 13845-51-7; HS_6^-, 60789-13-1; S_6^{2-}, 12597-13-6; H_2S_7, 12026-48-1; HS_7^-, 60789-14-2; S_7^{2-}, 60789-15-3; H_2S_8, 60789-16-4; HS_8^-, 60789-17-5; S_8^{2-}, 12764-43-1; $HSSO_3H$, 14921-76-7; $HSSO_3^-$, 20386-50-9; SSO_3^{2-}, 14383-50-7; HS_2SO_3H, 14616-61-6; $HS_2SO_3^-$, 16393-45-6; ${}^-S_2SO_3H$, 60815-95-4; ${}^-S_2SO_3^-$, 52895-34-8; HS_3SO_3H, 32480-93-6; $HS_3SO_3^-$, 44588-04-7; ${}^-S_3SO_3H$, 60789-18-6; ${}^-S_3SO_3^-$, 60789-19-7; HS_4SO_3H, 60789-20-0; $HS_4SO_3^-$, 44659-02-1; ${}^-S_4SO_3H$, 60789-21-1; ${}^-S_4SO_3^-$, 60789-22-2; HS_5SO_3H, 60789-23-3; $HS_5SO_3^-$, 44826-97-3; ${}^-S_5SO_3H$, 60789-24-4; ${}^-S_5SO_3^-$, 60789-25-5; HS_6SO_3H, 60789-26-6; $HS_6SO_3^-$, 44933-46-2; ${}^-S_6SO_3H$, 60789-27-7; ${}^-S_6SO_3^-$, 60789-28-8; $H_2S_3O_6$, 27621-39-2; $S_3O_6^{2-}$, 15579-17-6; $H_2S_4O_6$, 13760-29-7; $S_4O_6^{2-}$, 15536-54-6; $H_2S_5O_6$, 14700-26-6; $S_5O_6^{2-}$, 15579-16-5; $H_2S_6O_6$, 14939-13-0; $S_6O_6^{2-}$, 31294-89-0; $H_2S_7O_6$, 28638-92-8; $S_7O_6^{2-}$, 31294-90-3; $HSO_2(OH)$, 7782-99-2; HSO_3^-, 60789-29-9; SO_3^{2-}, 14265-45-3; $(HO)_2SO$, 7782-99-2; $SO_2(OH)^-$, 15181-46-1.

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Bis(trifluoromethyl)sulfimide, Bis(trifluoromethyl)-*N*-alkylsulfimides, and Bis(trifluoromethyl)-*N*-alkylsulfoxyimides

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Bis(trifluoromethyl)sulfimide, $(CF_3)_2S{=}NH$, results when ammonia and bis(trifluoromethyl)sulfur difluoride, $(CF_3)_2SF_2$, are allowed to react in the presence of benzylamine. With primary amines, the corresponding bis(trifluoromethyl)-*N*-alkylsulfimides, $(CF_3)_2S{=}NR$ ($R = CH_3$, C_2H_5, i-C_3H_7), are formed. At reduced temperature, the sulfimide and *N*-alkylsulfimides are oxidized with *m*-chloroperbenzoic acid to the corresponding sulfoxyimide, $(CF_3)_2S(O){=}NH$, and *N*-alkylsulfoxyimides, $(CF_3)_2S(O){=}NR$.

The chemical behavior of bis(trifluoromethyl)sulfur difluoride, $(CF_3)_2SF_2$,[1] differs markedly from that of its more highly fluorinated analogues CF_3SF_3 and SF_4. A qualitative comparison of the hydrolytic stability of these compounds shows that the ease of hydrolysis decreases in the order $SF_4 > CF_3SF_3 > (CF_3)_2SF_2$. While SF_4 fumes in moist air[2,3] and CF_3SF_3 hydrolyzes in water readily at 25 °C,[4,5] $(CF_3)_2SF_2$ can be stored in the presence of a large excess of water at 25 °C for at least 1 week with no apparent hydrolysis occurring. A similar difference in reactivity occurs with anhydrous ammonia where with SF_4 reaction proceeds even at −95 °C[3] whereas with $(CF_3)_2SF_2$ no reaction takes place even upon heating.[1]

We now report that $(CF_3)_2SF_2$ will undergo metathesis reactions with primary amines to produce a series of new bis(trifluoromethyl)-*N*-alkylsulfimides, $(CF_3)_2S{=}NR$. These moderately stable compounds are oxidized readily by using *m*-chloroperbenzoic acid (MCPBA) to form the bis(trifluoromethyl)-*N*-alkylsulfoxyimides, $CF_3S(O){=}NR$.[6]

Also, we find that, in the presence of a primary amine, the reaction of ammonia and bis(trifluoromethyl)sulfur difluoride does occur readily to form the stable bis(trifluoromethyl)sulfimide, $(CF_3)_2S{=}NH$.[7] Oxidation of the latter with MCPBA at low temperature gives bis(trifluoromethyl)sulfoxyimide which was reported previously.[6]

Results and Discussion

Bis(trifluoromethyl)sulfur difluoride, $(CF_3)_2SF_2$, undergoes metathetical reactions with primary amines to produce a series of new *N*-alkylsulfimides

$$(CF_3)_2SF_2 + 3RNH_2 \rightarrow (CF_3)_2S{=}NR + 2RNH_2{\cdot}HF$$
$$R = CH_3, C_2H_5, i\text{-}C_3H_7;\ R \neq H$$

These reactions proceed very rapidly at 25 °C. In some cases, if the rate of warming from −196 to +25 °C is too rapid, discoloration occurs and lower yields result. Based on the ease with which the above reactions occur, the fact that ammonia does not react is somewhat unexpected. However, when a primary amine is added to the NH_3–$(CF_3)_2SF_2$ mixture, reaction does occur to produce bis(trifluoromethyl)sulfimide, $(CF_3)_2S{=}NH$, in reasonable yield

$$(CF_3)_2SF_2 + NH_3 \xrightarrow[R = C_6H_5CH_2]{RNH_2} (CF_3)_2S{=}NH\ (50\text{–}60\%)$$

Other primary amines can be used in this reaction, also. When methylamine is used, the $(CF_3)_2S{=}NH$ is formed in only trace quantities. Better yields are obtained when isopropylamine is utilized, but the product, bis(trifluoromethyl)-*N*-isopropylsulfimide, from the competing reaction is separated from $(CF_3)_2S{=}NH$ with considerable difficulty. Because of its low volatility, $(CF_3)_2S{=}NCH_2C_6H_5$, which is certainly formed, has not been isolated.

The new bis(trifluoromethyl)sulfimide is more stable than its hydrocarbon analogue $(CH_3)_2S{=}NH$ which was reported to be stable at −30 °C and to decompose slowly at 0 °C.[8] The inherent instability of $F_2S{=}NH$ with respect to NSF and HF probably precludes its isolation as a stable species at 25 °C, although many of its derivatives are known and are stable.[9] Bis(trifluoromethyl)sulfimide is stable at 25 °C for extended periods in Pyrex glass but decomposes slowly at 35 °C. Decomposition in glass is rapid at 60 °C. When the compound was mixed with dry air and allowed to stand at room temperature for 1 week, only trace amounts of impurities were observed.

An unexpected side reaction, which results in the formation of CF_3H, occurs in the reactions of $(CF_3)_2SF_2$ with primary amines. In the case where $R = i$-C_3H_7, significant amounts of $CF_3SN(H)CH(CH_3)_2$[10] are also found. The reduction of S^{VI} to S^{IV} is accompanied by concomitant C–S bond breaking.