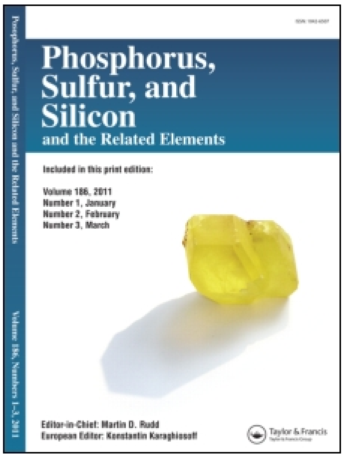

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THE PHOTOELECTRON SPECTRA OF METHANESULFENYL CHLORIDE AND METHANESULFENYL BROMIDE

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THE PHOTOELECTRON SPECTRA OF METHANESULFENYL CHLORIDE AND METHANESULFENYL BROMIDE

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The He(I) photoelectron spectra of methanesulfenyl chloride, CH_3SCl, and methanesulfenyl bromide, CH_3SBr, have been obtained by analysis of the gas-phase products of the reaction of methyl mercaptan, CH_3SH, with the respective halogens. The experimental ionization potentials correlate well with calculated molecular orbital eigenvalues and show that the S—Cl bond involves greater $p\pi$–$p\pi$ interaction than the S—Br bond.

INTRODUCTION

Methanesulfenyl chloride, CH_3SCl, is a reactive compound which decomposes in the liquid state at room temperature.[1] However, at low pressures it is stable over a sufficient period to allow a wide range of gas-phase studies. Its geometry, quadrupole coupling constants, dipole moment and internal rotation barrier have been thoroughly investigated by microwave spectroscopy.[2–4] The infrared and Raman spectra[5] and the ultraviolet absorption spectrum[6] have also been obtained.

Photoelectron (PE) spectroscopy provides a most direct means of studying the electronic structure of reactive molecules. A number of sulfur–chlorine compounds have been studied by He(I) PE spectroscopy. These include sulfur dichloride, SCl_2,[7] and disulfur dichloride, S_2Cl_2.[8] CH_3SCl has been used to generate thioformaldehyde, CH_2S, for study by PE spectroscopy.[9]

Methanesulfenyl chloride can be prepared by the chlorination of methylmercaptan or dimethyl disulphide using chlorine or sulfuryl chloride in the liquid or vapor phase.[4,6] Methanesulfenyl bromide, CH_3SBr, on the other hand, has not been studied spectroscopically, probably because of its lower stability, though it has been prepared in solution.[10]

We have measured the He(I) PE spectra of CH_3SCl and CH_3SBr as the major product of the low pressure room temperature gas phase reaction of CH_3SH with Cl_2 and Br_2, respectively.

EXPERIMENTAL

Chlorine (at −80°C) (or bromine (at −5°C)) and methyl mercaptan (at −80°C), held in glass tubes, were admitted simultaneously through Teflon needle valves to an all-glass reaction chamber. The gaseous reaction products passed directly to the glass inlet nozzle placed in the ionization chamber of the photoelectron spectrometer. The operation of the computer-controlled spectrometer has been described previously.[11] The incomplete reaction of Cl_2 with CH_3SH results in a spectrum of the reactants with the products CH_3SCl and HCl. The reaction of Br_2 with CH_3SH is much faster and stoichiometric amounts of the reactants produces a spectrum only of the products, CH_3SBr and HBr.

RESULTS AND CALCULATIONS

The time-averaged He(I) spectrum of the CH_3SH/Cl_2 reaction products is shown in Figure 1a. By stripping the appropriately measured spectra of CH_3SH, Cl_2 and HCl from this spectrum, the He(I) spectrum of "pure" CH_3SCl is obtained as shown in Figure 1b. Similarly the time-averaged He(I) spectrum of the CH_3SH/Br_2 reaction products, shown in Figure 2a, is stripped of the product HBr to give the spectrum of "pure" CH_3SBr shown in Figure 2b.

In molecular orbital (MO) terms a total of seven *p*-based PE bands are expected in the ionization potential (IP) region below about 18 eV. This is the case for both CH_3SCl and CH_3SBr as indicated in the spectra of Figures 1b and 2b, respectively. The measured vertical IPs are given in Table I. Since

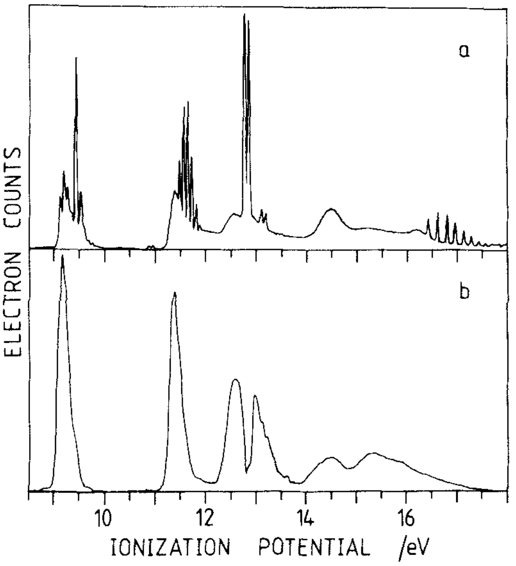

FIGURE 1 HE(I) photoelectron spectra of (a) the mixed spectrum of CH_3SH/Cl_2 and their reaction products, and (b) the stripped spectrum of CH_3SCl.

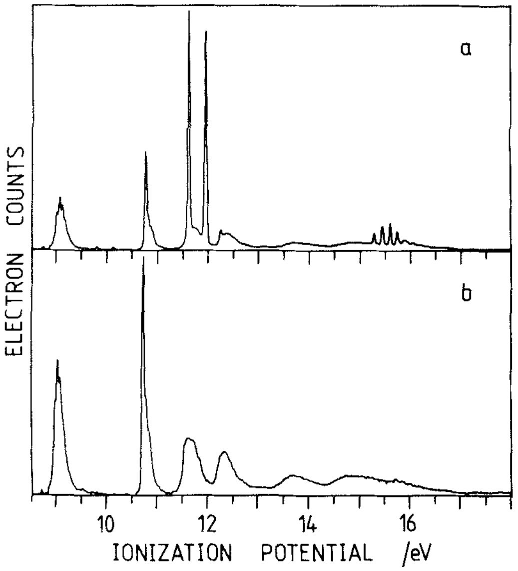

FIGURE 2 HE(I) photoelectron spectra of (a) the mixed spectrum of the CH_3SH/Br_2 reaction products, and (b) the stripped spectrum of CH_3SBr.

TABLE I

Comparison of experimental vertical ionization potentials and calculated VEOMP eigenvalues (in eV) for CH_3SCl and CH_3SBr

CH_3SCl			CH_3SBr		
IP[a]	MO[b]	ε[c]	IP[a]	MO[b]	ε[c]
9.21	$5a''$	−8.83	9.05	$8a''$	−8.23
11.37	$16a'$	−10.32	10.74	$22a'$	−9.05
12.55	$15a'$	−11.33	11.66	$21a'$	−9.92
12.93	$4a''$	−11.56	12.35	$7a''$	−10.10
14.39	$14a'$	−12.92	13.72	$20a'$	−12.20
15.19	$3a''$	−15.95	14.85	$6a''$	−15.77
15.61	$13a'$	−16.00	15.66	$19a'$	−15.78

[a] Accuracies vary between ±0.03 and ±0.10 eV.
[b] For C_s symmetry.
[c] For the STO-3G valence basis.

these molecules are iso-valence-electronic with the halamines CH_3NHCl and CH_3NHBr, similarities in their He(I) PE spectra[12,13] are expected. The second PE band in these latter molecules is a very sharp band associated with the highly localized non-bonding halogen electrons, n_x. The similar second band in CH_3SBr indicates the presence of a localized n_{Br} orbital, but in CH_3SCl the second band appears to be somewhat broadened, which if correct, suggests a greater degree of S—Cl interaction involving the corresponding n_{Cl} orbital.

These observations can be studied by means of appropriate molecular orbital calculations on CH_3SCl and CH_3SBr. A Gaussian 70[14] minimum basis STO-3G calculation has been made for CH_3SCl using its experimental geometry.[4] A recently developed valence-electron-only model potential (VEOMP) method[15,16] based on the all-electron Gaussian 70 program, and using a minimum valence STO-3G basis, has been used in comparative calculations on CH_3SCl and CH_3SBr, the latter involving an assumed equilibrium geometry.[17]

The VEOMP method is non-empirical and involves a valence-electron Hamiltonian including a core pseudopotential and screening function. It is able to produce orbital energies and equilibrium geometries in good agreement with the corresponding all-electron calculations, in particular for small molecules of first- and second-row atoms.[15,16] The minimum *sp* valence basis VEOMP-3G program has recently been extended to include third-row *p*-block atoms.[18]

The VEOMP eigenvalues and MO assignments for CH_3SCl and CH_3SBr are given in Table I, where they show good correlation with the experimental vertical IPs. For CH_3SCl the all-electron STO-3G calculation gives the same MO order and eigenvalues which show a mean difference of 0.32 eV compared to the VEOMP values.

DISCUSSION

Whereas the assignment of the ionization potentials of CH_3SCl and CH_3SBr are the same in terms of the order of symmetries, the absence of the sharp second band in CH_3SCl compared to that in CH_3SBr, which seems clearly to be associated with localized n_{Br} character, leads to a consideration of likely differences in orbital compositions between the two molecules. Additional data from the VEOMP calculations which are of relevance are summarized in Table II. These include the MO compositions expressed as percentages of CH_3, S and halogen character, and the MO bonding parameters (defined as ρ_{AB} for the AB atom pair[13]) which are a theoretical measure of the bonding and antibonding character of each MO partitioned into the CH_3, CS and SX bonding regions.

For both molecules the VEOMP data shows that the first band is associated with n_s localized character with some antibonding admixture of the n_x halogen orbital of a'' symmetry. This matches the observed broader shape and lower IP of each first band in comparison with the first band of CH_3SH.[19] At the high IP end of each spectrum the close sixth and seventh bands are associated with CH_3 orbitals, strongly bonding and highly localized. These bands are also clearly associated with their analogs in the spectrum of CH_3SH, namely its fourth and fifth bands.[19] As well the third IP (13.64 eV) of CH_3SH which can be described as σ_{CS} bonding does correspond reasonably well, according to the data in Table II, with the fifth bands of CH_3SCl (14.39 eV) and CH_3SBr (13.72 eV).

TABLE II

VEOMP molecular orbital atomic compositions and bonding parameters for CH_3SCl and CH_3SBr

	Atomic compositions			Bonding parameters[a]		
	%CH_3	%S	%X	ρCH_3	ρCS	ρSX
CH_3SCl						
$5a''$	3	73	24	6	−10	−37
$16a'$	9	29	62	−1	9	−26
$15a'$	4	23	73	8	−5	32
$4a''$	3	19	78	6	−5	30
$14a'$	26	41	32	13	58	37
$3a''$	94	5	1	144	13	1
$13a'$	95	2	3	183	8	0
CH_3SBr						
$8a''$	2	53	45	5	−6	−35
$22a'$	4	10	86	−2	3	−12
$21a'$	4	35	61	8	−7	44
$7a''$	4	43	53	9	−8	30
$20a'$	33	53	14	9	64	20
$6a''$	95	5	0	173	12	0
$19a'$	96	2	2	177	7	0

[a] Using the ρ_{AB} formula defined in Ref. 13.

The remaining second, third and fourth bands are those which, according to Table II, do not correlate between CH_3SCl and CH_3SBr. Whereas the chlorine contributions are calculated as 62, 73 and 78%, respectively, in CH_3SCl, in CH_3SBr the bromine contributions are 86, 61 and 53%, respectively, showing an opposite trend. In this latter case the 86% Br character of the $22a'$ MO correlates excellently with the observed sharp second band and verifies its essentially bromine non-bonding character. As well the VEOMP MO bonding parameters reinforce this result.

The third (11.66 eV) and fourth (12.35 eV) bands of CH_3SBr are similar in shape and area which closely matches the data for the $21a'$ and $7a''$ MOs in Table II. These MOs are the two strongest in S—Br bonding character, and since the $7a''$ MO can only involve an overlap of strict π-symmetry, then the $21a'$ MO, though lying in the symmetry plane, must involve an overlap of valence p orbitals in an approximate π-like arrangement.

By comparison, the second, third and fourth bands of CH_3SCl are rather different in that they are of about equal halfwidths and none is obviously of chlorine lone-pair character. The third (12.55 eV) and fourth (12.93 eV) bands are relatively close and hence likely to be of different symmetry. The order of IPs, $15a' < 4a''$, suggested by the VEOMP calculation could be in error since the calculation separates these by only 0.23 eV. Though of mainly chlorine character, both these MOs are reasonably S—Cl bonding. However, the second band at 11.37 eV is separated by over 1 eV from the third band, which is well-matched by the calculation in that the corresponding $16a'$ MO is mainly of chlorine character but reasonably S—Cl antibonding.

That chlorine lone-pair character appears in each of these three MOs appears to be due to the similar electronegativity of the interacting chlorine and sulfur orbitals, as well as the fact that, being adjacent elements of the second-row their orbital overlaps are maximized. The similar electronegativities are indicated by the appropriate IPs of CH_3SH (second IP of 12.02 eV) and HCl (first IP of 12.80 eV) or CH_3Cl (first IP of 11.31 eV).

A more relevant comparison using related molecules involves dimethyl sulfide, $(CH_3)_2S$, and sulfur dichloride, SCl_2. However, the correlations between the IPs of CH_3SCl and those of $(CH_3)_2S$[20] and

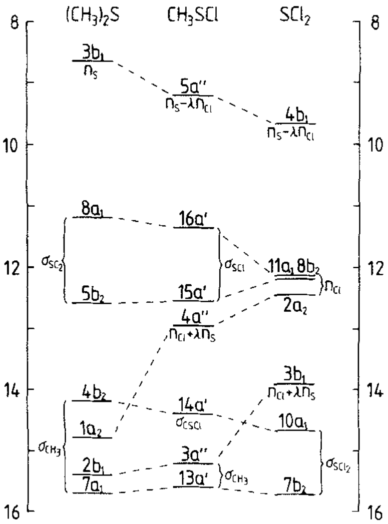

FIGURE 3 Correlation diagram for the experimental ionization potentials (in eV) of $(CH_3)_2S$, CH_3SCl and SCl_2. Data are from references 7 and 20.

SCl_2[7] are complicated by the higher C_{2v} symmetry and a lack of simple IP correlations for these latter molecules. The correlation diagram shown in Figure 3 includes obvious relationships between the first IPs, of n_s character in each case, and the σ_{CH_3} IPs of $(CH_3)_2S$ and CH_3SCl. The σ_{CSCl} IP of CH_3SCl (14.39 eV) falls between the σ_{SC_2} IPs of $(CH_3)_2S$ (mean 11.9 eV) and the σ_{SCl_2} IPs of SCl_2 (mean 15.2 eV). In the 11–13 eV region, the three IPs of CH_3SCl relate to the σ_{SC_2} of $(CH_3)_2S$ and the n_{Cl} IPs of SCl_2, though direct correlations cannot be drawn.

A simple correlation between these three molecules is offered by application of IP sum rules.[21] The a' and a'' partial sums are compared with the $a_1 + b_2$ and $a_2 + b_1$ partial sums of $(CH_3)_2S$ and SCl_2 and their means, as follows:

	$(CH_3)_2S$	SCl_2	Mean		CH_3SCl
$\sum a_1 + b_2$	53.70	54.75	54.22	$\sum a'$	53.92
$\sum a_2 + b_1$	38.85	36.03	37.44	$\sum a''$	37.33
Totals	92.55	90.78	91.66		91.55

The CH_3SCl partial and total sums are each marginally higher than the mean of the corresponding sums for $(CH_3)_2S$ and SCl_2. Any variation in the assignment of IPs for CH_3SCl worsens the agreement between these two sets of sums.

CONCLUSION

The He(I) PE spectra of CH_3SCl and CH_3SBr show interesting differences arising from the stronger interaction between S and Cl valence orbitals compared with the S—Br interactions. Whereas CH_3SCl has been widely studied by other forms of molecular spectroscopy, the present study represents the first spectroscopic investigation on methanesulfenyl bromide, CH_3SBr.

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17. For CH_3SBr the assumed geometry is that of CH_3SCl (Ref. 4) amended with a S—Br bondlength of 2.237 Å.
18. For bromine the VEOMP parameters for $\zeta_{4s} = \zeta_{4p} = 2.3523$ are, as defined in Ref. 16, $a_4 = 4.277$. $\Delta\varepsilon_C{}^A$ 1*s* 459.059, 2*s* 58.124, 2*p* 53.665, 3*s* 7.536, 3*p* 5.795 and 3*d* 1.436, for valence eigenvalues $\varepsilon_{4s} = -0.8040$ and $\varepsilon_{4p} = -0.3693$ in a.u.
19. Our measured IPs for CH_3SH differ slightly with those obtained by other workers (Ref. 20). We obtain I_1 9.44 (a''), I_2 12.02 (a'), I_3 13.64 (a'), I_4 15.12 (a'') and I_5 15.55 (a') in eV.
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