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Mass Spectra, Appearance Potentials, Heats of Formation, and Bond Energies of Some Alkyl and Perfluoroalkyl Sulfides

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A series of related alkyl and perfluoroalkyl sulfides and disulfides has been studied by electron impact in a mass spectrometer. From appearance potential and subsidiary thermochemical data the upper limits of their heats of formation are derived, as is done for the principal fragment ions and radicals, and estimates of the C–S and S–S bond strengths are made.

Introduction

The earliest classical thermochemical studies of simple alkanethiols and alkane sulfides date back to the work of Thomsen in 1886.[1] Since then many people have entered the field as organic sulfur compounds became important in petroleum technology and in rubber and protein chemistry. To supplement thermochemical data on these compounds, other workers began to study them using electron impact techniques.

In 1952, Franklin and Lumpkin[2] determined the C–S and S–S bond energies in dimethyl sulfide and dimethyl disulfide, respectively. They found the two bonds to have equal strength (73.2 kcal/mol). Later in a study of the heats of combustion and vaporization of the same two compounds, Mackle and Mayrick[3] discovered that the S–S bond was 5 kcal/mol weaker than the C–S bond and suggested that the electron impact processes be restudied. Palmer and Lossing[4] and later Gowenlock, Kay, and Majer[5] supported this finding with their electron impact data. Other values for these bond strengths have also been reported and the highest value obtained is 77.3 kcal/mol for both.[6]

Peters[7] showed that the ionization energy of a lone-pair s atomic orbital is virtually independent of the molecular environment of the atom. However, this is not true of p atomic orbital lone-pair electrons. It is usual to regard the bonding in sulfides and polysulfides as involving two bonding p orbitals with the remaining lone pairs on the sulfur atom occupying s and p orbitals. Bent[8] suggested that the greater the electronegativity of the groups attached to sulfur, the more nearly will the bond angle approach that predicted for p_2 geometry.

In this work, a series of six related sulfides and disulfides substituted with methyl and trifluoromethyl groups was studied. Data are presented on their mass spectra, heats of formation, fragment appearance potentials, and C–S and S–S bond strengths. Substitution of the more electronegative trifluoromethyl groups

causes significant changes in bond dissociation energies. The ionization potentials (IP's) of these molecules have been previously determined by photoelectron spectroscopy.[9] Substituting a methyl group with a more electronegative one should give more p character to the lone pair which loses its electron on ionization, and thus the first IP could be expected to decrease on increasing trifluoromethyl substitution. Instead the reverse is found, indicating that the inductive effect on the lone pair is greater than the rehybridization effect. Using Bent's ideas[8] this could also be ascribed to an increase in the electronegativity of the sulfur atom on substitution by electronegative groups. The first IP's of these molecules as determined by electron impact in the present investigation show the same trends.

Experimental Section

All the compounds were prepared by methods described in the literature[10,11] or were purchased from commercial sources. The mass spectra were obtained using an AEI MS9 mass spectrometer, with a modified source control such that appearance potentials could be obtained. The relevant ionization efficiency curve and that of a standard (usually krypton or xenon) were treated as described by Warren.[12] The ion accelerating potential was 8 keV and the electron trap current 100 μA using 70-V electrons. The source temperature was about 250°.

Results

All energes are given in electron volts. Tables I–VI show the mass spectra and appearance potentials of the principal ions of the sulfides and disulfides.[13,14] Peaks arising from different isotopes of sulfur and carbon are labeled (i). The percentage abundances were calculated with the largest peak in the spectrum as reference. Peaks with percentage abundances less than 3 are not reported. The number of determinations is also included to give an indication of the re-

(1) J. Thomsen, "Thermochemische Untersuchungen," Vol. IV, J. A. Barth, Leipzig, 1886.
(2) J. L. Franklin and H. E. Lumpkin, *J. Amer. Chem. Soc.*, **74**, 1023 (1952).
(3) H. Mackle and R. G. Mayrick, *Trans. Faraday Soc.*, **58**, 33 (1962).
(4) T. F. Palmer and F. P. Lossing, *J. Amer. Chem. Soc.*, **84**, 4661 (1962).
(5) B. G. Gowenlock, J. Kay, and J. R. Majer, *Trans. Faraday Soc.*, **59**, 2463 (1963).
(6) T. L. Allen, *J. Chem. Phys.*, **31**, 1039 (1959).
(7) D. Peters, *J. Chem. Soc.*, 2901 (1964).
(8) H. A. Bent, *Can. J. Chem.*, **38**, 1235 (1960).

(9) W. R. Cullen, D. C. Frost, and D. A. Vroom, *Inorg. Chem.*, **8**, 1803 (1969).
(10) H. C. Clark, *Advan. Fluorine Chem.*, **3**, 619 (1963).
(11) W. R. Cullen and P. S. Dhaliwal, *Can. J. Chem.*, **45**, 379 (1967).
(12) J. W. Warren, *Nature*, **165**, 810 (1950).
(13) In the determination of the appearance potentials, the kinetic energy and excitation energy terms are neglected. The appearance potentials therefore give an upper limit for the energy required for ion formation. Other factors such as those introduced in the interpretation of the efficiency curves for the ion under study and the calibrating gas and the energy distribution of the electron beam affect the accuracy of the measured appearance potentials. However, electron impact results for fragment ions are usually reliable to about 0.1 or 0.2 eV.[14]
(14) F. H. Field and J. C. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957.

TABLE I
MASS SPECTRUM AND APPEARANCE POTENTIALS OF THE PRINCIPAL IONS OF $(CH_3)_2S$ (eV)

m/e	Ion (% abundance)	Predicted processes[a]	No. of determinations	AP
15	CH_3^+ (5.8)	$\rightarrow CH_3^+ + SCH_3$	6	$\sim 10^b$
27	$C_2H_3^+$ (17.0)	$\rightarrow C_2H_3^+ + (SH_3)$	3	15.02 ± 0.10
34	SH_2^+ (28.6)	$\rightarrow SH_2^+ + (C_2H_4)$	5	14.29 ± 0.04
45	CHS^+ (25.3)	$\rightarrow CHS^+ + CH_3 + H_2$	5	14.16 ± 0.08
46	CH_2S^+ (32.2)	$\rightarrow CH_2S^+ + CH_3 + H$	10	10.97 ± 0.13
47	CH_3S^+ (75.5)	$\rightarrow CH_3S^+ + CH_3$	10	11.09 ± 0.15
48	CH_3SH^+ (5.4)			
49	$CH_3SH_2^+$ (5.5)			
61	$CH_3SCH_2^+$ (33.5)	$\rightarrow CH_3SCH_2^+$	10	11.95 ± 0.16
62	$CH_3SCH_3^+$ (100)	$\rightarrow CH_3SCH_3^+$	10	8.76 ± 0.18

[a] Refers to fragmentation of parent. [b] First break in the efficiency curve occurs at ~ 14 eV.

TABLE II
MASS SPECTRUM AND APPEARANCE POTENTIALS OF THE PRINCIPAL IONS OF CH_3SSCH_3 (eV)

m/e	Ion (% abundance)	Predicted processes[a]	No. of determinations	AP
15	CH_3^+ (4.6)	$\rightarrow CH_3^+ + SSCH_3$	10	$\sim 10^b$
44	CS^+			
45	CHS^+ (34.6)	$\rightarrow CHS^+ + CH_4S + H$	10	13.43 ± 0.09
46	CH_2S^+ (24.7)	$\rightarrow CH_2S^+ + CH_4 + S$	8	10.61 ± 0.11
47	CH_3S^+ (20.4)	$\rightarrow CH_3S^+ + CH_3S$	10	11.23 ± 0.11
48	CH_3SH^+ (11.7)	$\rightarrow CH_4S^+ + CS + H_2$	5	9.72 ± 0.09
49	$CH_3SH_2^+$ (4.5)	$\rightarrow CH_4S^+ + CS + H_2$	5	11.44 ± 0.15
61	$CH_3SCH_2^+$ (12.6)	$\rightarrow C_2H_5S^+ + SH$	10	10.66 ± 0.05
62[c]	$CH_3SCH_3^+$ (4.7)		5	8.96 ± 0.06
64	S_2^+ (8.6)	$\rightarrow S_2^+ + 2CH_3$	10	15.01 ± 0.13
76	CS_2^+ (7.7)			
78	$CH_2S_2^+$ (3.2)			
79	CH_3SS^+ (49.2)	$\rightarrow CH_3SS^+ + CH_3$	10	11.73 ± 0.24
80	CH_3SSH^+ (3.2)			
81	$CH_3SSH_2^+$ (5.3)			
93	$CH_3SSCH_2^+$			
94	$CH_3SSCH_3^+$ (100)	$\rightarrow CH_3SSCH_3^+$	10	8.85 ± 0.20

[a] Refers to fragmentation of parent. [b] First break in efficiency curve occurs at ~ 12.9 eV. [c] Probably from $(CH_3)_2S$.

TABLE III
MASS SPECTRUM AND APPEARANCE POTENTIALS OF THE PRINCIPAL IONS OF CH_3SCF_3 (eV)

m/e	Ion (% abundance)	Predicted processes[a]	No. of determinations	AP
15	CH_3^+ (12.3)	$\rightarrow CH_3^+ + SCF_3$	3	14.24 ± 0.13
44	CS^+ (4.1)			
45	CHS^+ (29.6)	$\rightarrow CHS^+ + CF_3 + H_2$	6	14.88 ± 0.06
46	CH_2S^+ (16.1)	$\rightarrow CH_2S^+ + CF_3 + H$	9	~ 14
47	CH_3S^+ (64.5)	$\rightarrow CH_3S^+ + CF_3$	5	11.78 ± 0.03
48	CH_3SH^+ (2.3)			
49	$CH_3SH_2^+$ (3.4)			
63	CSF^+ (11.8)	$\rightarrow CSF^+ + CH_3 + F_2$	5	15.32 ± 0.13
66	CH_3SF^+ (2.4)			
69	CF_3^+ (51.6)	$\rightarrow CF_3^+ + SCH_3$	5	13.07 ± 0.09
76	CS_2^+ (4.6)			
82	SCF_4^+ (5.1)			
97	$CH_3SCF_2^+$ (7.5)	$\rightarrow CH_3SCF_2^+ + F$	5	15.7 ± 0.24
115	$CH_2SCF_3^+$ (7.9)			
116	$CH_3SCF_3^+$ (100)	$\rightarrow CH_3SCF_3^+$	5	9.75 ± 0.11

[a] Refers to fragmentation of parent.

TABLE IV
MASS SPECTRUM AND APPEARANCE POTENTIALS OF THE PRINCIPAL IONS OF CH_3SSCF_3 (eV)

m/e	Ion (% abundance)	Predicted processes[a]	No. of determinations	AP
15	CH_3^+ (4.3)	$\rightarrow CH_3^+ + CF_3 + SS$	2	$\sim 10^b$
45	CHS^+ (21.1)	$\rightarrow CHS^+ + CSF_3 + H_2$	6	14.83 ± 0.08
46	CH_2S^+ (12.1)	$\rightarrow CH_2S^+ + SH + CF_3$	6	13.43 ± 0.24
47	CH_3S^+ (10.5)	$\rightarrow CH_3S^+ + S + CF_3$	6	12.84 ± 0.11
63	CFS^+ (3.5)			
64	S_2^+ (10.2)			2.46
69	CF_3^+ (22.6)	$\rightarrow CF_3^+ + CH_3SS$	5	12.50 ± 0.08
78	CH_2SS^+ (8.0)			
79	CH_3SS^+ (63.7)	$\rightarrow CH_3SS^+ + CF_3$	6	11.29 ± 0.20
80	CH_3SSH^+ (2.8)			
81	$CH_3SSH_2^+$ (6.5)			
82	CF_2S^+ (8.0)			
94	$CH_3SSCH_3^+$ (5.3)	$\rightarrow CH_3SSCH_3^+$	3	9.27 ± 0.08
129	$CH_3SSCF_2^+$ (3.4)	$\rightarrow CF_3SSCF_2^+ + F$	5	~ 15
133	CF_3SS^+ (5.3)	$\rightarrow CF_3SS^+ + CH_3$	6	14.77 ± 0.12
148	$CH_3SSCF_3^+$ (100)	$\rightarrow CH_3SSCF_3^+$	6	9.58 ± 0.14

[a] Refers to fragmentation of parent. [b] First break in the efficiency curve occurs at ~ 14 eV.

TABLE V
MASS SPECTRUM AND APPEARANCE POTENTIALS OF THE PRINCIPAL IONS OF $(CF_3)_2S_2$ (eV)

m/e	Ion (% abundance)	Predicted processes[a]	No. of determinations	AP
31	CF^+ (2.5)	$\rightarrow CF^+ + SSCF_3 + F_2$	1	~ 16
32	S^+ (3.4)	$\rightarrow S^+ \bullet SCF_3 + CF_3$	1	~ 13
44	CS^+ (3.3)			
63	CFS^+ (4.8)			
64	S_2^+ (14.8)	$\rightarrow S_2^+ + 2CF_3$	6	13.22 ± 0.17
69	CF_3^+ (100)	$\rightarrow CF_3^+ + SSCF_3$	10	12.07 ± 0.13
76	CS_2^+ (21.0)			
82	CF_2S^+ (12.1)	$\rightarrow CF_2S^+ + CF_3S + F$	5	10.93 ± 0.17
95	$CFSS^+$ (4.8)	$\rightarrow CFSS^+ + CF_3 + F_2$	5	15.60 ± 0.10
101	CF_3S^+ (4.8)	$\rightarrow CF_3S^+ + SCF_3$	6	14.43 ± 0.08
114	CF_2SS^+ (20.6)	$\rightarrow CF_2SS^+ + CF_4$	5	11.28 ± 0.06
133	CF_3SS^+ (22.5)	$\rightarrow CF_3SS^+ + CF_3$	6	13.31 ± 0.05
183	$CF_2SSCF_3^+$ (10.7)	$\rightarrow CF_3SSCF_2^+ + F$	5	14.64 ± 0.07
202	$CF_3SSCF_3^+$ (84.4)	$\rightarrow CF_3SSCF_3^+$	8	10.68 ± 0.19

[a] Refers to fragmentation of parent.

TABLE VI
APPEARANCE POTENTIALS OF THE PRINCIPAL IONS OF $(CF_3)_2S$ (eV)

m/e	Ion	Predicted processes[a]	No. of determinations	AP
69	CF_3^+	$\rightarrow CF_3^+ + SCF_3$	5	12.54 ± 0.06
151	$CF_3SCF_2^+$	$\rightarrow CF_3SCF_2^+ + F$	1	~ 15
170	$CF_3SCF_3^+$	$\rightarrow CF_3SCF_3^+$	5	11.28 ± 0.04

[a] Refers to fragmentation of parent.

liability and reproducibility of the appearance potential values quoted. Table VII lists heats of formation of reactants and products of the electron-induced reactions calculated using the appearance potential data and predicted processes shown in Tables I–VI. The calculations were made as in the following examples.

In the reaction $CH_3SCH_3 \rightarrow CH_3S^+ + CH_3$, ΔH_f $(CH_3SCH_3) = \Delta H_f(CH_3S^+) + \Delta H_f(CH_3) - AP$ (CH_3S^+/CH_3SCH_3). Using the literature values for $\Delta H_f(CH_3SCH_3)^{4,15}$ and $\Delta H_f(CH_3)$,[16] $\Delta H_f(CH_3S^+) \leq \Delta H_f(CH_3SCH_3) - \Delta H_f(CH_3) + AP(CH_3S^+/CH_3SCH_3)$ $\leq -0.39 - 1.41 + 11.09 \leq 9.29$ eV. With this derived heat of formation, the heat of formation of SCH_3 can be obtained from $CH_3SSCH_3 \rightarrow CH_3S^+ + SCH_3$ where $\Delta H_f(SCH_3) = \Delta H_f(CH_3SSCH_3) - \Delta H_f(CH_3S^+) + AP(CH_3S^+/CH_3SSCH_3) \leq -0.25 - 9.29 + 11.23 \leq 1.69$ eV. The value for $\Delta H_f(CH_3SSCH_3)$ is taken from the work of Hubbard and coworkers.[15] Literature

(15) W. N. Hubbard, D. R. Douslin, J. P. McCullough, D. W. Scott, S. S. Todd, J. F. Messerly, I. A. Hossenlopp, A. George, and G. Waddington, *J. Amer. Chem. Soc.*, **80**, 3547 (1958).

(16) F. P. Lossing in "Mass Spectrometry," C. A. McDowell, Ed., McGraw-Hill, New York, N. Y., 1963.

TABLE VII

HEATS OF FORMATION OF SULFIDES AND FRAGMENTS OBTAINED BY ELECTRON IMPACT (UPPER LIMITS) (eV)

Species	Parent	ΔH_f	Species	Parent	ΔH_f
	CH_3SCH_3	12.36 ± 0.3	CH_3S	CH_3SSCH_3	1.69 ± 0.3
CHS^+	CH_3SCF_3	12.39 ± 0.4	CF_3S	CH_3SCF_3	-4.70 ± 0.4
	CH_3SSCH_3	11.49 ± 0.4	CH_3SS	CH_3SSCH_3	1.31 ± 0.4
	CH_3SSCF_3	11.67 ± 0.5	CF_3SS	CF_3SSCF_3	-6.23 ± 0.4
CH_3S^+	CH_3SCH_3	9.29 ± 0.2	S_2	CH_3SSCH_3	1.94 ± 0.4
CH_3SS^+	CH_3SSCH_3	10.07 ± 0.3		CF_3SSCF_3	1.28 ± 0.4
	CH_3SSCF_3	8.13 ± 0.4	CH_3SCF_3	a	-7.58 ± 0.4
CH_4S^+	CH_3SSCH_3	7.13 ± 0.3	CF_3SCF_3	b	-12.23 ± 0.4
$CH_3SCH_3{}^+$	CH_3SCH_3	8.37 ± 0.2	CH_3SSCF_3	c	-8.25 ± 0.4
$CH_3SSCH_3{}^+$	CH_3SSCH_3	8.60 ± 0.2	CF_3SSCF_3	d	-13.29 ± 0.4
$S_2{}^+$	CH_3SSCH_3	12.74 ± 0.2			
	CH_3SSCF_3	12.08 ± 0.4			
CF_3S^+	CF_3SSCF_3	5.84 ± 0.4			
CF_3SS^+	CF_3SSCF_3	5.11 ± 0.4			
$CH_3SCF_3{}^+$	CH_3SCF_3	2.17 ± 0.4			
$CH_3SSCF_3{}^+$	CH_3SSCF_3	1.33 ± 0.4			
$CF_3SCF_3{}^+$	CF_3SCF_3	-0.95 ± 0.4			
$CF_3SSCF_3{}^+$	CF_3SSCF_3	-2.61 ± 0.4			

a From ΔH_f of CH_3S^+ and CF_3.   *b* From ΔH_f of $CF_3{}^+$ and SCF_3.   *c* From ΔH_f of CH_3S^+ and SCF_3.   *d* From ΔH_f of CF_3SS^+ and CF_3.

values of the heats of formation of CF_3 and CF_3^+ [17] and CH_3^+ [16] were used.[18]

Using the derived heats of formation of the neutral molecules and radicals, the different S–C and S–S bond strengths can be compared. A typical calculation of the upper limit of the bond dissociation energy of the CF_3–$SSCF_3$ bond in bis(trifluoromethyl) disulfide follows. For the reaction $CF_3SSCF_3 \rightarrow CF_3 + SSCF_3$, $\Delta H_f(CF_3SSCF_3) = \Delta H_f(CF_3) + \Delta H_f(SSCF_3) - D(CF_3\text{–}SSCF_3)$. Therefore $D(CF_3\text{–}SSCF_3) = \Delta H_f(CF_3) + \Delta H_f(SSCF_3) - \Delta H_f(CF_3SSCF_3) \leq -5.09 + (-6.23) - (-13.29) \leq 1.97$ eV. The bond energies calculated in this manner are presented in Table VIII.

TABLE VIII

C–S AND S–S BOND ENERGIES (UPPER LIMITS) (eV)

⌐———CH₃–S———¬		⌐———CF₃–S———¬		⌐———S–S———¬	
Parent	Bond energy	Parent	Bond energy	Parent	Bond energy
$CH_3\text{–}SCH_3$	3.49				
$CH_3\text{–}SCF_3$	4.29	$CH_3S\text{–}CF_3$	4.18		
		$CF_3S\text{–}CF_3$	2.44		
$CH_3\text{–}SSCH_3$	2.97			$CH_3S\text{–}SCH_3$	3.63
$CH_3S\text{–}SSCF_3$	3.41	$CH_3SS\text{–}CF_3$	4.47	$CH_3S\text{–}SCF_3$	5.24
		$CF_3SS\text{–}CF_3$	1.97	$CF_3S\text{–}SCF_3$	3.89

Discussion

Mass Spectra of Dimethyl Sulfide and Dimethyl Disulfide.—The percentage abundances of the fragment peaks obtained from dimethyl sulfide and dimethyl disulfide differ slightly from those previously reported.[5,19] This could be due to different experimental conditions, in particular, source temperature[20] and also of course the general mass spectrometer design.

The spectrum of the monosulfide shows a peak at m/e 34 $(AP(SH_2^+) = 14.29 \pm 0.04$ eV). The AP value is comparable to that previously reported for SH_3^+ (AP = 13.85 eV)[5] and the relative abundance of

the ions in the two spectra indicates that they may in fact be the same species. Other workers have reported a peak at m/e 35.[21] However, in the present investigation an accurate mass determination of m/e 34, 33.9486 (calcd for SH_2, 33.9877), confirms our assignment.

The high value of the AP of the m/e 27 peak in the spectrum of the monosulfide (15.02 $\pm$ 0.10 eV) indicates that this is a rearrangement peak. Accurate mass measurement shows that the fragment is $C_2H_3^+$, and the AP agrees with the previous value of 14.7 eV.[5] The peak at m/e 62 from the disulfide is probably due to monosulfide impurity or monosulfide produced by thermal decomposition of the disulfide in the ion source since its AP is only 0.21 eV above the IP of dimethyl sulfide.

Mass Spectra of All Compounds.—The ionization potentials of the parent molecules determined in this investigation are, as expected, slightly higher than those values obtained by the more reliable photoionization technique.[9] The electron impact IP of dimethyl sulfide (8.76 $\pm$ 0.18 eV) is higher than one value previously reported (8.70 $\pm$ 0.2 eV)[22] but lower than another (9.0 eV).[5] The IP of dimethyl disulfide (8.85 $\pm$ 0.2 eV) is slightly lower than that reported by Hobrock and Kiser (9.1 eV).[19] The effect of the trifluoromethyl groups on the IP's of sulfides has been mentioned in the Introduction.

The spectra of all compounds with S–CH_3 bonds have a peak at m/e 15 and the ion efficiency curves have a long tail rendering it very difficult to obtain an accurate value for the AP. In the case of dimethyl disulfide there is a break in the curve at 12.9 eV which corresponds to the ionization–dissociation process: $CH_3SSCH_3 + e^- \rightarrow CH_3^+ + SSCH_3 + 2e^-$. An estimate of 10 $\pm$ 0.5 eV for the AP of CH_3^+ from the monosulfide can be made which indicates that the ion may be formed by ionization of the free radical resulting from

(17) C. E. Melton and W. H. Hamill, *J. Chem. Phys.*, **41**, 546 (1964).

(18) The accuracy of the data in Tables VII and VIII is very dependent on the accuracy of the heats of formation of CH_3SCH_3, CH_3^-, etc., and on the appearance potential data. The errors are estimated.

(19) B. G. Hobrock and R. W. Kiser, *J. Phys. Chem.*, **66**, 1648 (1962).

(20) C. E. Brion, *Anal. Chem.*, **37**, 1706 (1965).

(21) E. J. Levy and W. A. Stahl, *ibid.*, **33**, 707 (1961).

(22) B. G. Hobrock and R. W. Kiser, *J. Phys. Chem.*, **67**, 1283 (1963).

thermal decomposition in the ion source. There is a sudden change in slope in the ionization efficiency curve around 14 eV indicating the presence of another process. This is probably $CH_3SCH_3 + e^- \rightarrow CH_3^+ + SCH_3 + 2e^-$.

The parent molecule ion gave the largest peak in all the spectra except those of compounds containing two trifluoromethyl groups. The particular stability of the trifluoromethyl group accounts for its prominence in the cracking pattern of compounds containing such a group. This also accounts for the relatively high percentage abundance of the S_2^+ peak in the spectrum of bis(trifluoromethyl) disulfide. The heat of formation of S_2 is calculated to be ≤ 1.94 eV using the data from dimethyl disulfide. This is slightly higher than the 1.34 eV reported by Evans and Wagman[23] and may indicate that the S_2^+ ion is formed in an excited vibrational state. Similar calculations using the appearance potential of S_2^+ from bis(trifluoromethyl) disulfide taking the most probable reaction as $CF_3SSCF_3 \rightarrow S_2^+ + 2CF_3$ give $\Delta H_f(S_2^+) = \Delta H_f(CF_3SSCF_3) - 2\Delta H_f(CF_3) + AP(S_2^+/CF_3SSCF_3) \leq 10.29$ eV which is lower than the $IP(S_2)$ of 10.8 eV.[24] This would give $\Delta H_f(S_2) \leq -0.51$ eV. If the S_2^+ ion is produced from the reactions $CF_3SSCF_3 \rightarrow CF_3 + SSCF_3$ and $CF_3SS \rightarrow S_2^+ + CF_3$, $\Delta H_f(S_2^+) = \Delta H_f(CF_3SS) - \Delta H_f(CF_3) + AP(S_2^+/CF_3SS) \leq 12.08$ eV. This gives $\Delta H_f(S_2) = 12.08 - 10.8 \leq 1.28$ eV, which is in fair agreement with 1.34 eV[23] and supports the fact that there is thermal decomposition in the ion source or that S_2^+ does not come from the parent molecule. The AP of CF_3^+ from this compound (Table IV) indicates that it is not formed by thermal decomposition followed by ionization.

The complete mass spectrum of bis(trifluoromethyl) sulfide is not reported since the sample contained a relatively high percentage of the disulfide. The monosulfide is prepared by irradiating the disulfide with ultraviolet light.[10]

Appearance and Ionization Potentials of Fragments.—The ionization potential of the CH_3S radical is calculated to be ≤ 7.60 eV using the data of Table VII. This is about 0.4 eV lower than the 8.06 ± 0.1 eV reported by Palmer and Lossing.[4] The value is lower than the IP of a sulfur atom[25] and probably results from a "backward" flow of charge from the CH_3 group. The IP of CH_3SS is similarly calculated to be ≤ 9.67 eV using the value of $\Delta H_f(CH_3SS^+)$ obtained from dimethyl disulfide. A value of ≤ 6.81 eV is obtained for the IP of the same species if the value from methyl(trifluoromethyl) disulfide is used. The bond strength of CH_3–$SSCH_3$ (2.97 eV) is less than that of CF_3–$SSCH_3$ (4.47 eV) (Table VIII); thus the difference in AP's, and hence IP's, may correspond to the energy required to separate CH_3SS^+ from CH_3SSCH_3, which is formed from CH_3SSCF_3 by rearrangement.

The fragment CHS^+ is obtained from methyl(trifluoromethyl) sulfide, dimethyl disulfide, and methyl(trifluoromethyl) disulfide. The derived $\Delta H_f(CHS^+)$ values (Table VII) for the two disulfides agree reasonably well. Hobrock and Kiser[19] reported a much higher value for the AP of CHS^+ which leads to a $\Delta H_f(CHS^+)$ of 12.96 eV, which seems to be higher than that obtained for the same fragment from dimethyl sulfide and methyl(trifluoromethyl) sulfide (Table VII).

The high and low values in this case are probably not significantly different and the mean of the values in Table VII, 12.0 eV, is more meaningful. This is close to other values reported by Hobrock and Kiser.[19,26]

The AP of the ion $CH_3SSCH_3^+$ in the spectrum of methyl(trifluoromethyl) disulfide is 0.52 eV higher than the IP of CH_3SSCH_3 indicating that the ion may be produced by some rearrangement in the ion source.

Heats of Formation and Bond Energies.—The heats of formation of the sulfides increase dramatically as CH_3 groups are replaced by CF_3 (Table VII), since the heats of formation of dimethyl sulfide and disulfide are -0.39 and -0.25 eV, respectively.[15]

As pointed out in the Introduction other investigators have found that the S–S bond strength in dimethyl disulfide is less than that of the C–S bond in dimethyl sulfide by about 4 kcal/mol.[3–5] The reverse is indicated from the present results (Table VIII) although the difference may not be significant. Other values for the CH_3S–CH_3 bond energy are slightly lower at 3.17,[2] 3.16,[3] 3.18,[4] and 3.21 eV.[5] The CH_3S–SCH_3 bond energies reported elsewhere range from 2.91[3] to 3.17 eV.[2] In the bis-trifluoromethyl compounds the difference between the C–S and S–S bond strengths is much greater, being 1.45 eV.

In both the sulfide and disulfide series, the C–S and S–S bonds are strongest when the molecule is asymmetrical, that is, when both CH_3 and CF_3 groups are present. This may be because of an increase in conjugation along the chains due to contributions from extreme VB forms such as $H^+H_2C=S=CF_2F^-$ and $H^+H_2C=S^+=S^-=CF_2F^-$, since one end is an electron-withdrawing group and the other is electron donating. $D(CF_3S-SCH_3)$ is found to be 5.24 eV which is higher than the 4.4 eV quoted for S_2.[24] The apparent similarity of the S–S bond strengths of the two other compounds is surprising since any delocalization would be expected to be at a minimum in bis(trifluoromethyl) disulfide resulting in a lowered bond strength.

In both the dimethyl and bis-trifluoromethyl series, the C–S bond is stronger in the monosulfide. This is due to the greater stabilities of the dissociated products of the disulfides; $\Delta H_f(SSCH_3) = 1.37$ eV compared with $\Delta H_f(SCH_3) = 1.69$ eV and $\Delta H_f(SSCF_3) = -6.23$ eV compared with $\Delta H_f(SCF_3) = -4.70$ eV, the other products being the same. The low C–S bond energy in the bis-trifluoromethyl compounds correlates with the fact that the SCF_3^+ ions are formed with very low intensity. Bis(trifluoromethyl) disulfide has a par-

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ticularly low C–S bond energy (1.97 eV) and preliminary results indicate that this may be a useful source of CF_3 radicals.[27]

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Studies of Pentavalent Organoarsenic, -antimony, and -bismuth Halide Compounds by Nuclear Quadrupole Resonance Spectroscopy

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The ^{75}As, $^{121,123}Sb$, ^{209}Bi, $^{35,37}Cl$, and $^{79,81}Br$ nqr spectra have been recorded in pentavalent organo group Va halide compounds having stoichiometry R_3MX_2, where R = CH_3, $C_6H_5CH_2$, and C_6H_5; X = F, Cl, and Br; and M = As, Sb, and Bi. All compounds studied, except for trimethylarsenic dibromide, appear to have trigonal-bipyramidal geometry in the solid state with idealized D_{3h} symmetry. $(CH_3)_3AsBr_2$ may be saltlike as $(CH_3)_3AsBr^+Br^-$ with the cation having C_{3v} symmetry. Electronic inductive effects have been interpreted in all compounds in terms of variation in the p orbital occupation in the group Va elements and the halogens. Nucleophilic character of the constituent atoms and groups is as follows: Bi > Sb > As, Br > Cl > F, and $CH_3 > C_6H_5CH_2 > C_6H_5$. Data for the pentavalent arsenic compounds are compared to those in R_3As where R = C_6H_5 and $C_6H_5CH_2$. The extra pair of electrons in As(III) compared to As(V) possesses considerable p character which helps to explain the pyramidal geometry assumed in the R_3As compounds.

Introduction

Arsenic, antimony, and bismuth form a series of pentavalent compounds having the stoichiometry R_3MX_2 where R may be alkyl or aryl groups and X the halides. Since all of the above three group Va elements and several of the halogens have quadrupole nuclei, nuclear quadrupole resonance spectroscopy is likely to be very useful in further elucidating the chemistry of these compounds. Until now, however, few nqr data have appeared concerning this particular class of compounds. Parker[2a] recorded the halogen and several antimony resonances in $(CH_3)_3SbX_2$ (X = Cl, Br, I) compounds. Macalady[2b] began preliminary studies on triphenylantimony dichloride but the several resonances he found were measured only approximately and no value of the electric field gradient asymmetry parameter could be determined. These data are apparently the only nqr results for Sb(V) organometallics heretofore reported. No ^{75}As resonances in pentavalent organoarsenic(V) compounds have been reported and, in fact, it appears that the only other As(V) resonance known is that in $Na_2HAsO_4 \cdot 7H_2O$.[3] The pentavalent state is an uncommon oxidation number for bismuth and the fact that no other Bi(V) nqr signals have been previously reported is not surprising. Barnes and Bray[4] found arsenic and antimony resonances in

$(C_6H_5)_3As$ and $(C_6H_5)_3Sb$. Robinson, Dehmelt, and Gordy[5] found bismuth resonances in $(C_6H_5)_3Bi$.

Muetterties and Phillips[6] have suggested that in pentacoordinate compounds of the R_3MX_2 type the more electronegative atoms (the halogens) are situated on the two apical positions of a trigonal-bipyramidal structure while the less electronegative groups link with the central atom at the three equatorial positions. The trigonal bipyramidal geometry has idealized D_{3h} point group symmetry according to Figure 1.

For the antimony compounds, Wells[7] has determined by X-ray diffraction that the $(CH_3)_3SbX_2$ compounds (X = Cl, Br, I) take on the idealized D_{3h} symmetry in the solid state. The nqr data[2a] are in agreement with this since the asymmetry parameter of the antimony electric field gradient is very close to zero. Polynova and Porai-Koshits[8] found that the structure of $(C_6H_5)_3$-$SbCl_2$ is also a trigonal bipyramid about the antimony atom. The ir spectra of the trimethylantimony dihalides[9] and triphenylantimony dihalides[10] are consistent with the D_{3h} point group. No data have been reported to date on the structural aspects of the tribenzylantimony dihalide compounds.

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