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NORMAL COORDINATE ANALYSIS OF TRIMETHYLANTIMONY OXIDE

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Summary

The infrared and Raman spectra of trimethylantimony oxide and its deuterated analogue were recorded. Assignments were made and a normal coordinate analysis was carried out. A polar coordinate linkage is proposed for the Sb—O bond.

Introduction

Although trialkylantimony compounds have been known for some time [1, 2], they have not been extensively studied. Infrared spectral studies of several triorganoantimonials have indicated that these molecules possess D_{3h} symmetry [3-7]. Of the infrared studies reported for monosubstituted triorganoantimony derivatives [3, 6, 8], only Shindo et al. [9] have studied a trimethylantimony compound, viz., trimethylantimony sulfide.

In the present work, trimethylantimony oxide was chosen for investigation. The $(CH_3)_3SbO$ molecule is the simplest of the triorganyl derivatives of antimony and logically fits into the systematic study of R_3MX compounds (M = As, Sb; X = O, S, Se). Recently we have reported the vibrational analyses for $(CH_3)_3AsS$ and $(CH_3)_3AsSe$ [10]. The nature of the Sb—O bond as compared to the other M—X bonds is also of considerable interest. In order to better understand the bonding, trimethylantimony oxide and its perdeuterated analog were synthesized and their infrared and Raman spectra were investigated. A normal coordinate calculation was carried out and force constants were determined. From these data, certain conclusions regarding the nature of the Sb—O bond were reached.

Experimental

The preparation of trialkylantimony oxides from the corresponding dihalides has been described in the literature [8, 22]. The trimethylantimony dibromide was prepared by the method of Hibbert [12]. This compound was then treated with silver oxide. The perdeuterated compound was prepared in a similar manner except that in the Grignard reaction, perdeuterated methyl iodide was used.

Trimethylantimony oxide-d_0 and -d_9 were prepared as highly crystalline, colorless solids by sublimation of the crude products at low pressures. The melting points (previously unreported) are 95-97°C and 101-102°C, respectively (uncorr.). The sublimed crystals analyzed as follows: C_3H_9SbO, found: C, 19.70; H, 4.96; calcd.: C, 19.63; H, 5.03%. C_3D_9SbO, found: C, 18.77; D, 9.45; calcd.: C, 18.77; D, 9.40%. The mid-infrared spectra were recorded in the form of KI pellets and as mulls in mineral oil or perfluorinated mineral oil using a Beckman model IR-12 double beam grating spectrophotometer. The Raman spectra of the solids were recorded by placing a few crystals of the compound into the sample holder of the Cary model 82 Raman spectrophotometer and using the 5145 Å line from a Coherent Radiation Model 53 argon ion laser as the exciting source. No solution spectra were recorded since a suitable solvent which would not react with the compound could not be found.

High resolution mass spectra were recorded on a CEC 21-110 B High Resolution Mass Spectrometer. These spectra demonstrated the strong tendency of $(CH_3)_3SbO$ molecules to be associated in the vapor phase.

Assignments of molecular vibrations

Trimethylantimony oxide-d_0 and -d_9 were assumed to possess C_{3v} symmetry. There are 36 normal vibrations resulting in 24 fundamental frequencies ($8A_1$ + $4A_2$ + $12E$). The A_1 and E vibrations are infrared and Raman active. The A_2 vibrations are infrared and Raman inactive but are expected to have frequencies virtually identical to those of the corresponding A_1 and E modes. This is due to the weakness of the interactions between different methyl groups [10]. The 24 frequencies are composed of 6 frequencies ($3A_1$ + $3E$) which arise from skeletal vibrations and 18 frequencies ($5A_1$ + $4A_2$ + $9E$) which are due to the motions of the methyl hydrogens (or deuteriums). The frequencies arising from the methyl vibrations may be divided into six CH_3 (or CD_3) stretching frequencies ($2A_1$ + A_2 + $3E$), six CH_3 (or CD_3) deformation frequencies ($2A_1$ + A_2 + $3E$), four CH_3 (or CD_3) rocking frequencies (A_1 + A_2 + $2E$), and two CH_3 (or CD_3) torsional frequencies (A_2 + E). Due to the lack of interaction between the methyl groups the separation between frequencies of different symmetry species is often immeasurably small. The skeletal vibrations give rise to two SbC_3 stretching frequencies (A_1 + E), two SbC_3 deformation frequencies (A_1 + E), one SbO stretching frequency (A_1), and one CSbO bending frequency (E).

The spectra of $(CH_3)_3SbO$ and $(CD_3)_3SbO$ are complicated by the fact that trimethylantimony oxide has considerable association with neighbouring molecules. The mass spectrum for $(CH_3)_3SbO$ showed extensive dimerization in the vapor phase (Fig. 2). The association of triorganylantimony oxides has been reported by Chremos and Zingaro [22]. What this means is that not only are monomer bands seen in the vibrational spectra, but also bands from associated forms. Since the associated molecules will, for the most part, have bonding similar to that of the monomer, a number of the fundamental frequencies appear as superpositions of two or more bands (broad bands) rather than single

TABLE 1

INFRARED AND RAMAN SPECTRA OF $(CH_3)_3SbO$ (cm^{-1})

Infrared				Raman		Assignment[a]
Solid		Mull		Solid		
Freq.	Rel. int.	Freq.	Rel. int.	Freq.	Rel. int.	
3016	m	3007	m	3012	16	$\nu_a(CH_3)$
2931	m	2920	m	2920	76	$\nu_s(CH_3)$
				2798	2	
1561	m			1553	vw	
1421	m			1415	vw	$\delta_a(CH_3)$
1310	m	1313	w			
1231	m	1230	m	1231	5	$\delta_s(CH_3)$
1199	w	1199	w	1197	18	
				1191	11	
				1051	vw	
821	s	800	s	810	vw	$\rho(CH_3)$
				733	vw	
708	s	713	s	711	vw	$\nu(SbO)$
645	vs	644	vs			
				574	14	$\nu_a(SbC_3)$
553	s	551	s	554	34	
526	s	524	s	517	100	$\nu_s(SbC_3)$
485	m					
				455	vw	
415	m					
				307	vw	
253	s			250	vw	$\delta_a(SbC_3)$
		222	s	227	vw	
		184	w	187	7	$b(CSbO)$
		173	m	170	24	$\delta_s(SbC_3)$
		105	m			
		99	w			ν_L
				74	5	
				41	vw	

[a] ν_a = antisym. stretch, ν_s = sym. stretch, δ_a = antisym. deformation, δ_s = sym. deformation, ρ = rock, b = bend, ν_L = lattice mode.

peaks. In addition, the associated forms add a few bands to other regions of the spectrum. The extra bands arising from the presence of non-monomeric forms can be seen in Tables 1 and 2 which list the observed infrared and Raman frequencies of $(CH_3)_3SbO$ and $(CD_3)_3SbO$. The assignments for the frequencies, which for the most part are taken from the sharper Raman lines, are summarized in Table 3.

It is useful to augment measurements made on the solid with solution data. However, such studies were hampered by the exceedingly hygroscopic nature of the compound (leading to the formation of $(CH_3)_3Sb(OH)_2$), its reaction with solvents (e.g., formation of $R_3Sb(OR')_2$ in alcohols [22]), or the very limited solubility in a variety of organic solvents. These difficulties also made it impossible to acquire acceptable molecular weight measurements. Saturated, but dilute solutions in CS_2 did serve to corroborate the assignment of ν_s(Sb—O).

CH_3 (and CD_3) stretching modes. The Raman bands at 3012 and 2920

TABLE 2

INFRARED AND RAMAN SPECTRA OF $(CD_3)_3SbO$ (cm^{-1})

Infrared				Raman		Assignment[a]
Solid		Mull		Solid		
Freq.	Rel. int.	Freq.	Rel. int.	Freq.	Rel. int.	
2258	m	2250	vw	2254	9	$\nu_a(CD_3)$
2150	m	2145	w	2110	75	$\nu_s(CD_3)$
				2018	vw	
1360	m	1342	w			
1161	m	1154	w	1150	vw	$\delta_a(CD_3)$
1041	s	1034	m	1040	vw	
948	s	950	m	942	18	$\delta_s(CD_3)$
				930	39	
846	s	846	w			
791	s					
761	vs	769	m			
726	s			728	vw	
628	vs	625	m	625	vw	$\nu(SbO)$
596	vs	594	m			$\rho(CD_3)$
546	vs	544	m			$\nu_a(SbC_3)$
528	vs	525	m	525	vw	
				505	36	
481	s	479	m	468	100	$\nu_s(SbC_3)$
454	s					
				425	vw	
408	s					
		258	s			$\delta_a(SbC_3)$
		214	m			
		177	m			b(CSbO)
		169	m			
		157	s	153	48	$\delta_s(SbC_3)$
				70	vw	ν_L

[a] As Table 1.

cm^{-1} with infrared mull counterparts at 3007 and 2920 cm^{-1} are assigned to the antisymmetric ($A_1 + A_2 + 2E$) and the symmetric ($A_1 + E$) stretching modes, respectively (2254 and 2110 cm^{-1} for the deuteride). These values agree quite well with the reported values for trimethylantimony dicarboxylates [5], dihalides [6], trimethylarsine sulfide [10], and selenide [10].

CH_3 (and CD_3) deformation modes. The antisymmetric deformation frequencies ($A_1 + A_2 + 2E$) are assigned to the Raman band at 1415 cm^{-1} (1421 cm^{-1} for the IR of the solid) and the symmetric frequencies ($A_1 + E$) to the Raman band at 1197 cm^{-1} and infrared band at 1199 cm^{-1}. For the deuterated compound the Raman bands occur at 1040 and 930 cm^{-1}. These values agree with those reported for the dihalides [6], the dinitrate [3, 4], the dicarboxylates [5], and the arsines [10]. The assignments for the deuterated compound are somewhat lower than those reported [6, 10], but agree with the values calculated for the isotopic shift.

CH_3 (and CD_3) rocking modes. All four methyl rocking frequencies ($A_1 + A_2 + 2E$) are assigned to the weak Raman band at 810 cm^{-1}; the infrared counterpart is at 800 cm^{-1} for the mull. For the deuterated compound the very strong

TABLE 3

VIBRATIONAL ASSIGNMENTS OF TRIMETHYLANTIMONY OXIDE

	Approximate description of $(CX_3)_3SbO$ vibration	Freq. (cm^{-1})	
		X = H	X = D
A_1	CX_3 antisym. str. (i.p.)	3012	2254
	CX_3 sym. str. (i.p.)	2920	2110
	CX_3 antisym. def. (i.p.)	1415	1040
	CX_3 sym. def. (i.p.)	1197	930
	CX_3 rock (i.p.)	810	596
	SbO str.	645	628
	SbC_3 sym. str.	517	468
	SbC_3 sym. def.	170	153
A_2	CX_3 antisym. str. (i.p.)	3012	2254
	CX_3 antisym. def. (i.p.)	1415	1040
	CX_3 rock (i.p.)	810	596
	CX_3 torsion (i.p.)	—	—
E	CX_3 antisym. str. (o.p.)	3012	2254
	CX_3 antisym. str. (o.p.)	3012	2254
	CX_3 sym. str. (o.p.)	2920	2110
	CX_3 antisym. def. (o.p.)	1415	1040
	CX_3 antisym. def. (o.p.)	1415	1040
	CX_3 sym. def. (o.p.)	1197	930
	CX_3 rock (o.p.)	810	596
	CX_3 rock (o.p.)	810	596
	SbC_3 antisym. str.	554	525
	SbC_3 antisym. def.	227	214
	CSbO bend	187	177
	CX_3 torsion (o.p.)	—	—

596 cm^{-1} infrared band corresponds to the rocking. Although these values are lower than those previously reported, the strong infrared and weak Raman bands are expected from previous results [10].

CH_3 (and CD_3) torsional modes. The assignment of the two torsional frequencies (A_2 + E) was not made. Because these vibrations give rise to weak infrared bands at low frequencies, they are very often not observed for molecules of this type.

SbC_3 stretching modes. The antisymmetric stretching frequency (E) is assigned to the Raman band at 554 cm^{-1}; the very intense infrared band for the mull is at 551 cm^{-1}. The infrared and Raman spectra of $(CD_3)_3SbO$ both show bands at 525 cm^{-1}. The A_1 symmetric SbC_3 stretching mode clearly gives rise to the most intense Raman band in the spectrum, at 517 cm^{-1} for the normal compound and at 468 cm^{-1} for the deuterated one. These values agree quite well with the frequencies reported for related compounds [3-9]. The antisymmetric stretching frequency reported for the deuterated dibromide [6], 574 cm^{-1}, is much higher than the value reported in the work, but the frequency calculated from the force constants agrees with this lower value.

SbC_3 deformation modes. The antisymmetric deformation frequency (E) is assigned to the strong infrared band at 222 cm^{-1} and the weak Raman band at 227 cm^{-1} (the medium intensity infrared band is at 214 cm^{-1} for the $(CD_3)_3SbO$).

The symmetric deformation frequency (A_1) is assigned to the infrared band at 170 cm^{-1} (153 cm^{-1} for the deuteride).

SbO stretching mode. The single SbO stretching frequency (A_1) is assigned to the strong very broad infrared band at 645 cm^{-1} (628 cm^{-1} for the deuteride). This value is in good agreement with previous work [8]. Also, saturated solutions of trimethylantimony oxide in CS_2 showed a well defined band at 658-663 cm^{-1}. Hence, the assignment of this band to the ν(SbO) monomer can be made with some confidence. Unfortunately, the solubility of the compound in this solvent is so limited, that all other absorptions were too weak to be useful.

Although the infrared band is very strong, the Raman band is not observed for the hydrogen compound and is very weak for the deuteride.

CSbO bending mode. The single CSbO bending frequency (E) is assigned to the infrared band at 184 cm^{-1} (177 cm^{-1} for the deuteride); the Raman counterpart is at 187 cm^{-1}.

Lattice modes. The infrared and Raman bands at 105, 99, 74 and 41 cm^{-1} (70 cm^{-1} for the deuteride) are assigned to lattice modes.

Normal coordinate analysis

The Wilson *FG* [13] method was used to carry out the normal coordinate calculations. These were performed on an IBM 360/65 or a CDC 1604-A computer using the programs developed by Schachtschneider [14, 15].

C_{3v} symmetry was assumed for the molecules. Bond lengths of 1.09 for the C—H (or C—D) bond, 2.20 for the Sb—C bond, and 1.92 Å for the Sb—O bond were selected. The C—H bond length is one commonly accepted for alkanes. The Sb—C bond length was that reported by Wilkins and Sutton [17] for $(CF_3)_3Sb$. The Sb—O bond length* was calculated from Pauling's eqn. using the double-bond value of oxygen and half Sb—Sb value reported for the atomic radii considering the electronegativities of the atoms [17]. All angles were assumed to be tetrahedral (109.47°). The choice of tetrahedral angles, made in the absence of structrual data for trimethylantimony oxide, simplified calculations in later work. Any error resulting from this approximation will lead to relatively small errors in the normal coordinate calculations.

A set of 37 internal coordinates was chosen in order to take advantage of the symmetry of the molecule. There are 13 bond stretches and 24 valence angle bends (Fig. 1). The symmetry coordinates generated from this set of internal coordinates are identical with those chosen by Kolar et al. [10] for trimethylarsine sulfide and selenide.

The calculated G matrix was used with an initial set of force constants taken from trimethylarsine sulfide [10] to calculate an initial set of frequencies which were compared with the observed values. Since the calculated frequencies were in fairly good agreement with those observed, only a moderate refinement of force constants was needed to give a least squares fit of the calculated to the observed frequencies.

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* Ideally, the bond distances should be based on X-ray crystallographic data. We made an intensive effort, prior to this study, to prepare single crystals suitable for a single X-ray structure determination. Despite all our efforts, using a variety of solvents, sublimation, melts and other established methods, no effort to grow single crystals of $(CH_3)_3SbO$ was successful.

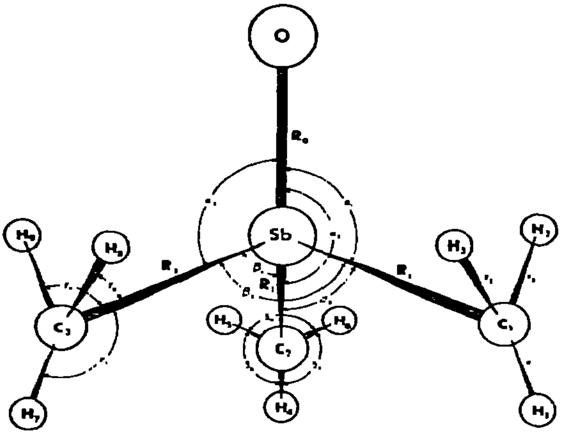


Fig. 1. Trimethylantimony oxide showing structure and internal coordinates.

The final set of valence force constants for the compounds are listed in Table 4. The potential energy distributions for the vibrational modes of each compound are given in Table 5.

TABLE 4

FORCE CONSTANTS FOR $(CH_3)_3SbO$

Symbol	Description	Value[a]
$f(R_0)$	Sb—O stretch	3.43
$f(R)$	Sb—C stretch	2.46
$f(r)$	C—H stretch	4.81
$f(\alpha)$	CSbO angle bend	0.67
$f(\beta)$	CSbC angle bend	0.71
$f(\gamma)$	SbCH angle bend	0.60
$f(\delta)$	HCH angle bend	0.55
$f(R_0R)$	Sb—O, Sb—C	0.08
$f(RR)$	Sb—C, Sb—C	—0.03
$f(rr)$	C—H, C—H	0.03
$f(\alpha\alpha)$	CSbO, CSbO	—0.03
$f(\beta\beta)$	CSbC, CSbC	—0.01
$f(\alpha\beta)$	CSbO, CSbC	—0.06
$f(\delta\delta)$	HCH, HCH	—0.01
$f(\gamma\gamma)$	SbCH, SbCH	0.15
$f(\gamma\delta)$	SbCH, HCH	0.13
$f(\beta\gamma)$	CSbC, SbCH	0.15
$f(\alpha\gamma)$	CSbO, SbCH	—0.07
$f(R_0\alpha)$	Sb—O, CSbO	0.25
$f(R_\alpha)$	Sb—C, CSbO	0.24
$f(R_\beta)$	Sb—C, CSbC	0.13
$f(R_\gamma)$	Sb—C, SbCH	0.29
$f(R_\delta)$	Sb—C, HCH	0.14
$f(r_\delta)$	C—H, HCH	—0.10

[a] Units: stretching force constants, mdyn/Å; bending force constants, mdyn · Å; stretching—bending force constants, mdyn.

TABLE 5

POTENTIAL ENERGY DISTRIBUTION FOR VIBRATIONS OF TRIMETHYLANTIMONY OXIDE

	$(CH_3)_3SbO$			$(CD_3)_3SbO$		
	Frequency (cm^{-1})			Frequency (cm^{-1})		
	Obsd	Calcd	P.E.D.[a]	Obsd	Calcd	P.E.D.[a]
A_1	3012	3013	$\nu_a(CH_3)$ 0.99	2254	2254	$\nu_a(CD_3)$ 0.98
	2920	2922	$\nu_s(CH_3)$ 0.99	2110	2108	$\nu_s(CD_3)$ 0.98
	1415	1418	$\delta_a(CH_3)$ 0.97	1040	1040	$\delta_a(CD_3)$ 0.93
	1197	1201	$\delta_s(CH_3)$ 0.93	930	927	$\delta_s(CD_3)$ 0.80 $\nu_s(SbC_3)$ 0.12
	810	813	$\rho(CH_3)$ 0.94	596	596	$\rho(CD_3)$ 0.89
	645	636	$\nu(SbO)$ 1.00	628	637	$\nu(SbO)$ 0.97
	537	530	$\nu_s(SbC_3)$ 1.00	468	476	$\delta_a(SbC_3)$ 0.94
	170	170	$\delta_s(SbC_3)$ 0.74; $\delta_s(CH_3)$ 0.23	153	153	$\delta_s(SbC_3)$ 0.73; $\delta_s(CD_3)$ 0.23
A_2	3012	3013	$\nu_a(CH_3)$ 0.99	2254	2251	$\nu_a(CD_3)$ 0.98
	1415	1422	$\delta_a(CH_3)$ 0.97	1040	1034	$\delta_a(CD_3)$ 0.96
	810	804	$\rho(CH_3)$ 0.99	596	590	$\rho(CD_3)$ 0.98
		—	—	—	—	—
E	3012	3013	$\nu_a(CH_3)$ 0.99	2254	2254	$\nu_a(CD_3)$ 0.98
	3012	3013	$\nu_a(CH_3)$ 0.99	2254	2252	$\nu_a(CD_3)$ 0.98
	2920	2922	$\nu_s(CH_3)$ 1.00	2110	2108	$\nu_s(CD_3)$ 0.98
	1415	1418	$\delta_a(CH_3)$ 0.97	1040	1039	$\delta_a(CD_3)$ 0.94
	1415	1417	$\delta_a(CH_3)$ 0.97	1040	1035	$\delta_a(CD_3)$ 0.95
	1197	1198	$\delta_s(CH_3)$ 0.93	930	927	$\delta_s(CD_3)$ 0.94
	810	812	$\rho(CH_3)$ 0.95	596	597	$\rho(CD_3)$ 0.91
	810	810	$\rho(CH_3)$ 0.96	596	593	$\rho(CD_3)$ 0.92
	544	565	$\nu_a(SbC_3)$ 1.00	525	512	$\nu_a(SbC_3)$ 0.94
	227	226	$\delta_a(SbC_3)$ 0.82	214	215	$\delta_a(SbC_3)$ 0.89
	187	191	b(CSbO) 0.83; $\delta_s(SbC_3)$ 0.10	177	172	b(CSbO) 0.88
	—	—	—	—	—	—

[a] P.E.D. = potential energy distribution; the fraction that the diagonal force constant of each symmetry coordinate contributes to the vibration.

Discussion

The potential energy distributions for trimethylantimony oxide-d_0 and -d_9 show that a relatively small amount of coupling exists between the different symmetry coordinates for the compounds. Significant coupling is noted between the CSbO bending vibration and the SbC_3 symmetric deformation in the hydride, between the SbC_3 symmetric deformation and CH_3 (or CD_3) symmetric deformation, and between the CD_3 symmetric deformation and the SbC_3 symmetric stretch.

The success in fitting the calculated frequencies to the observed frequencies suggests that the assignments are reasonable and that the more significant force constants are included in the set of force constants used in the calculations. In most cases, the calculated frequencies are somewhat higher than the observed frequencies of $(CH_3)_3SbO$, but are lower in the case of $(CD_3)_3SbO$. This is an indication of the anharmonicity of the vibrations for which corrections have

TABLE 6

FORCE CONSTANTS FOR BOND STRETCHES (mdyn/Å) AND ANGLE BENDS (mdyn · Å)

Molecule	M—X	M—C	C—H	CMC	CMX	MCH
$(CH_3)_3NO$ [a]	3.90	3.71	4.92			
$(CH_3)_3PO$ [a]	8.25	3.19	4.85			
$(CH_3)_3AsO$ [a]	5.82	2.98	4.85			
$(CH_3)_3AsS$ [b]	2.94	2.94	4.80	0.63	0.69	0.56
$(CH_3)_3AsSe$ [b]	2.56	2.94	4.79	0.63	0.66	0.56
$(CH_3)_3SbO$ [c]	3.43	2.46	4.81	0.71	0.67	0.60

[a] Ref. 19. [b] Ref. 10. [c] This work.

not been made. The Teller—Redlich product rule [18], which is often useful in checking assignments, is of limited use for molecules containing torsions. This is due to the harmonicity assumptions made in its derivation. It can, however, be used to check the assignments of the frequencies in the A_1 symmetry block. The value calculated from the product rule is 5.56 while the value calculated from the observed frequencies is 5.75. This good agreement supports the assignments made for this symmetry block.

Table 6 compares the force constants for the three bond stretches and the four angle bends in $(CH_3)_3NO$, $(CH_3)_3PO$, and $(CH_3)_3AsO$ reported by Choplin and Kaufmann [19], and those reported by Kolar et al. [10] for $(CH_3)_3AsS$ and $(CH_3)_3AsSe$ with those of $(CH_3)_3SbO$ reported in this work. The values of the force constants for the C—H stretch are very similar (about 4.8 mdyn/Å). The values of the force constants for the M—C stretch and the M—O stretch are in a decreasing order as one proceeds down the family. The angle bending force constants in $(CH_3)_3SbO$ are only slightly higher than those reported for the arsines. Unfortunately, there are not sufficient data to observe any trends in these force constants. There is an indication that the nitrogen compound may need to be restudied to confirm the reported values.

A comparison of the frequencies assigned to the vibrations involving the M atom for several $(CH_3)_3MX$ molecules is given in Table 7. The decreasing frequencies of the vibrations as M gets heavier is expected. There is a good comparison of frequencies for the common vibrations of the antimony oxide and sulfide.

TABLE 7

FREQUENCIES (cm^{-1}) FOR $(CH_3)_3MX$

Molecule	ν(M—X)	ν_s(M—C)	ν_a(M—C)	$\delta_s(MC_3)$	$\delta_a(MC_3)$	b(CMX)
$(CH_3)_3NO$ [a]	935	765	945	466	490	364
$(CH_3)_3PO$ [a]	1148	666	743	317	364	264
$(CH_3)_3AsO$ [a]	868	590	636	256	275	217
$(CH_3)_3AsS$ [b]	462	596	632	213	213	196
$(CH_3)_3AsSe$ [b]	320	591	630	209	209	163
$(CH_3)_3SbS$ [c]	431	531	555	149	180	
$(CH_3)_3SbO$ [d]	645	517	554	170	227	187

[a] Ref. 19. [b] Ref. 10. [c] Ref. 9. [d] This work.

TABLE 8

BOND ORDERS FOR M—X IN $(CH_3)_3MX$

Molecule	Bond order [a]	Ref.
$(CH_3)_3NO$	0.63	19
$(CH_3)_3PO$	1.96	19
$(CH_3)_3AsO$	1.60	19
$(CH_3)_3AsS$	1.43	10
$(CH_3)_3AsSe$	1.40	10
$(CH_3)_3SbO$	1.20	this work

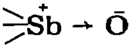
[a] Bond orders calculated from Gordy's rule.

Gordy's equation [20] may be used to estimate the bond order for the Sb—O bond. The equation is:

$$k = 1.67\, N(X_a X_b/d^2)^{0.75} + 0.30$$

where k is the stretching force constant ($\times\ 10^{-5}$) in dynes/cm, N is the bond order, X is the electronegativity of the atom, and d is the bond length in Å. From Pauling [17], $X_{Sb} = 1.9$ and $X_O = 3.5$. The Sb—O bond length is 1.92 Å and $k = 3.43 \times 10^5$ dynes/cm. The calculated bond order is 1.20. Bond orders of related compounds are compared in Table 8. The decrease in bond orders is quite obvious.

From Pauling's rules, the Sb—O bond is found to be about 47 per cent ionic [17] based upon the difference of electronegativity of the atoms. As a strong infrared band and a weak Raman band were observed, it appears that the



$$\gt\overset{+}{\text{Sb}} \rightarrow \bar{\text{O}}$$

double bond is a polar coordinate linkage as shown. This could also explain the results of a gaseous electron diffraction study of the molecular structures of $(CH_3)_3PY$ and $(CH_3)_3AsY$ (Y = O, S) which showed the oxides to have a M—O bond length shorter than expected for classical double bonding [21].

The mid-infrared spectra of trimethylantimony oxide-d_0 and -d_9 are characterized by broad bands and several strong and medium bands which cannot be assigned to the vibrations of the molecule. The Raman spectra also contain several unassigned bands. Since most of these bands are located at frequencies close to those of the oxides, the presence of impurities closely related in structure to that of the oxides was considered.

Elemental analyses of the samples show both to be of high purity. In an attempt to characterize the nature of any impurities, high resolution mass spectra of the samples were run. The mass spectral pattern of the perdeuterated compound is shown in Fig. 2 (the pattern of the protonated compound was identical). Unfortunately, no molecular ion peak was observed for either the monomeric or associated form of trimethylantimony oxide. The most intense peak is that of a dimer which has lost one methyl group. This particle was absolutely identified via high resolution measurements: for $C_5H_{15}O_2{}^{121}Sb_2$, exp.: 348.9165, calc.: 348.9146; for $C_5H_{15}O_2{}^{121}Sb^{123}Sb$, exp.: 350.9168, calc.: 350.9151, for $C_5H_{15}O_2{}^{123}Sb_2$, exp.: 352.9167, calc.: 352.9156. Also, the peak intensities

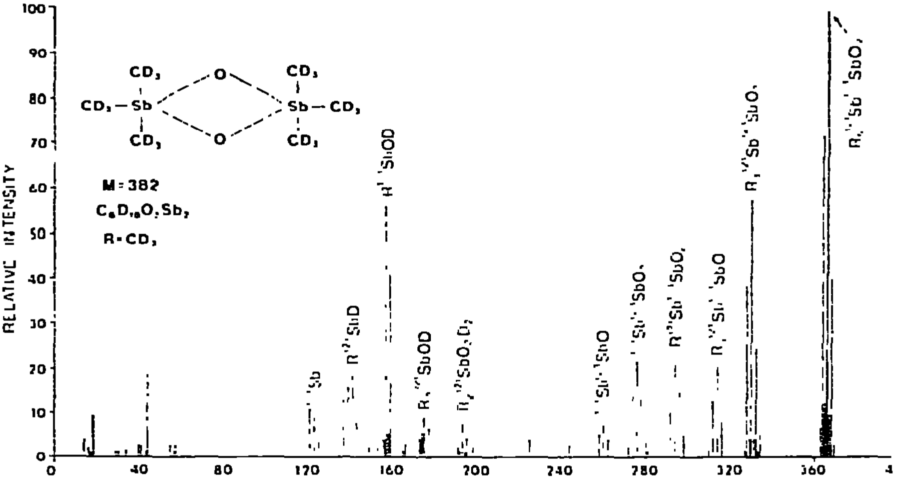


Fig. 2. Mass spectrum of trimethylantimony oxide-d_9

followed the statistical distribution predicted from the $^{121}Sb/^{123}Sb$ ratio. Several intense peaks are noted which contain two antimony and two oxygen atoms and are attributed to oxygen-bridged structures of the type drawn in Fig. 2. Those portions of the mass spectra which correspond to fragments of a dimeric form may arise directly from associated forms. However, this does not unequivocally establish the fact of the existence of a stable oxygen-bridged dimer either in the solid or gas phase. The dimer could also form by the association of a monomer molecule with a second monomer molecule which has lost one methyl group following electron impact.

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