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PREPARATION, PROPERTIES AND STRUCTURE OF POLY(TRIPHENYLSTIBINE OXIDE)*

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SUMMARY

Our results indicate that the best method for the preparation of poly(triphenylstibine oxide) is the oxidation of triphenylstibine in acetone with 30% hydrogen peroxide, followed by the removal of water and excess peroxide with refluxing benzene. A less preferred alternative method involves the hydrolysis of triphenylstibine dichloride with alcoholic potassium hydroxide and the subsequent heating of the isolated solid $(C_6H_5)_3Sb(OH)_2$ until no hydroxyl bands can be detected by infrared spectroscopy. Solubility, PMR, infrared, Raman, thermal (DTA and TGA), mass spectral, and X-ray powder data are reported. The products are readily identified by characteristic infrared and Raman absorptions in the region between 800 and 400 cm^{-1}. The mass spectral data, although inconclusive when trying to identify impurities in the samples, corroborate the polymeric nature of triphenylstibine oxide.

INTRODUCTION

Doak and Freedman[1] recently reviewed procedures reported to yield a product that was propounded to be triphenylstibine oxide. Incomplete and conflicting data make it difficult to ascertain from the earlier literature if the "triphenylstibine oxide" was the product obtained. Few, if any, analyses are included with the reported melting point of the product, which is the only physical property adaptable for comparisons. Spectroscopic data are noticeably absent in all but the most recent studies. Consequently, characterization of several materials identified as triphenylstibine oxide was undertaken to establish a positive reference for future work.

RESULTS AND DISCUSSION

Several methods as reported in the literature for the preparation of triphenyl-

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TABLE 1

ANALYTICAL DATA FOR PRODUCTS OBTAINED FROM REACTIONS INVESTIGATED FOR PREPARATION OF TRIPHENYLSTIBINE OXIDE

Product from reaction indicated	Analyses found (%)				M.p. (°C)
	C	H	Sb	O	
A $(C_6H_5)_3Sb+H_2O_2$	58.92	4.17	32.99	3.9[a]	280
B $(C_6H_5)_3Sb+H_2O_2$	58.4	4.2	32.3[a]	5.1	280
C $(C_6H_5)_3SbCl_2$ +KOH(EtOH)	58.2	4.1	32.6	5.1	280
D $(C_6H_5)_3SbBr_2$ +KOH(EtOH)	62.4	4.5	27.7[a]	5.4	217
E $(C_6H_5)_4SbOH$ +heat, xylene	64.5	4.4	29.1	2.0	238

[a] Value calculated by differences. $(C_6H_5)_3SbO$ calcd.: C, 58.53; H, 4.10; Sb, 32.99; O, 4.38%. $(C_6H_5)_4SbOH$ calcd.: C, 64.46; H, 4.73; Sb, 27.23; O, 3.58%.

stibine oxide were attempted. In general, these literature methods resulted in mixtures which contained insoluble products that were difficult or impossible to purify. Analyses of these materials were not consistent with any reasonable compound or compounds. However, the hydrolysis reaction of triphenylstibine dichloride, using the method reported herein, did yield a product that, based on the analytical results (Table 1), was consistent with the formula of triphenylstibine oxide. Furthermore, the product that was isolated from the oxidation of triphenylstibine with 30% hydrogen peroxide, using the procedure reported in this work, also was labeled triphenylstibine oxide (Table 1). Two other products, one from the hydrolysis of triphenylstibine dibromide and one from the thermal degradation of tetraphenylstibonium hydroxide, were not considered the desired oxide, but the two products were also included in our spectral investigations in an attempt to characterize possible impurities.

Although capillary melting points of products A, B, and C (Table 1) were approximately the same, 280–281°, the DTA thermograms did show differences. The thermogram of product A showed a possible melting at 310°, followed by an exothermic reaction indicating decomposition. Product C exhibited an endotherm at 275°, followed by an exotherm at 290°; an entirely different thermogram from product A, although the infrared spectra appear the same. If the heating was stopped after the decomposition appeared complete ($\approx$350°), an amber viscous liquid remained in the DTA tube. The identity of the liquid was not investigated. Products D and E had much lower endotherms (248° and 252°, respectively) than those for products that we have identified as triphenylstibine oxide. Thermal gravimetric analysis of products A and C at atmospheric pressure indicated loss of weight beginning at 290° and 215°, respectively, using a heating rate of 20°/min. Consequently, the relatively high decomposition temperatures of triphenylstibine oxide and the indicated temperatures for the beginning of weight loss suggested the use of mass spectral analysis as a possible means of identifying the isolated products.

The most striking difference between the mass spectral data of triphenylphosphine oxide[2,3], triphenylarsine oxide[3], on the one hand, and triphenylstibine oxide was the observation of m/e values greater than the molecular ion $(C_6H_5)_3MO^+$, in the latter compound. As the sample of triphenylstibine oxide was heated in the spectrometer[4], the appearance of peaks in the range of *m/e* 659 through 663 suggested that a polymeric material was decomposing into smaller, more volatile portions (Table 2). Minor differences were noted when the mass spectra of the various products listed in Table 1 were compared. Unfortunately, none of the differences could be used to distinguish between the products. Products D and E had mass spectra similar to triphenylstibine[3,5] except for weak peaks at *m/e* 368 and 370 (Ph_3SbO^+).

As a further aid in the comparison of the various triphenylstibine oxide products, X-ray powder photographs were taken of products B, C, D, and E; Table 3 gives the calculated "*d*-spacings." Products B and C can be judged to be essentially the same compound; whereas product D is quite different and is characterized by much larger *d*-spacings for low values of the reflection angle. In general, product E gave similar results to those of product D but with a slightly larger number of reflections. The comparatively smaller values of the interplanar spacings of products B and C suggest that triphenylstibine oxide may not be polymerized to a very high degree and as a result may possess a relatively small unit cell. A preliminary attempt to index the reflection quickly showed that triphenylstibine oxide does not have a cubic lattice.

The solubility of triphenylstibine oxide, product B in Table 1, was determined in several organic solvents. The solvent and solute were placed under nitrogen, sealed in a suitable vessel, kept at approximately 60° for seven days, and then kept at room temperature for one day. The weight of solid, which was not identified, in a sample of solution was determined by evaporating the solution to dryness, giving the following results:

Solvent	Grams of sample per liter of solution
CCl_4	8.4
$CHCl_3$	4.6
CH_2Cl_2	21.2 (probably reacted)
C_6H_6	6.4
CH_3OH	41.4 (probably reacted)

Extraction of triphenylstibine oxide (product A) in a Soxhlet extractor with dry, hot carbon tetrachloride for periods of four and eight days, did not alter the composition of the material left in the thimble. Infrared spectra and chemical analyses were consistent with triphenylstibine oxide (Found: C, 58.56; H, 4.10; Sb, 33.00%). A very small quantity of an insoluble material (m.p. 278°), which was isolated by filtering the carbon tetrachloride, appeared to be a mixture of products but predominantly the original oxide, and was not further analyzed. Evaporation of the two straw-colored carbon tetrachloride filtrates yielded a buff-colored solid (four days) melting between 268° and 276° (Found: C, 57.62; H, 4.55; Sb, 36.90; Cl, 0.00%), and a tan-colored solid (eight days) exhibiting no melting to 360° (Found: C, 31.37; H, 2.95; Sb, 53.44; Cl, 0.00%). The lability of the phenyl–antimony bond is noted by the suggested mixture of products formed: first, $(C_6H_5)_5Sb_2O$ (calcd.: C, 55.86; H, 3.81; Sb, 37.75%) and, after prolonged heating, $C_6H_5SbO_2$ (calcd.: C, 31.21; H,

TABLE 2

PRINCIPAL POSITIVE IONS IN THE MASS SPECTRUM OF POLY(TRIPHENYLSTIBINE OXIDE)

m/e	Relative intensity (%)	Ion	m/e	Relative intensity (%)	Ion
663	7	$Ph_5Sb_2O_2^+$	216	5	$PhSbO^+$
661	9		214	7	
659	7		200	66	$PhSb^+$
448	7	$Ph_2Sb_2O_3^+$	198	59	
446	8		155	15	Ph_2^+
444	7		154	59	
432	73	$Ph_2Sb_2O_2^+$	153	14	
430	100		152	13	
428	67		94	21	$C_6H_5OH^+$
370	8	Ph_3SbO^+	78	45	$C_6H_5^+$
368	11		77	45	
354	77	Ph_3Sb^+	51	31	$C_4H_3^+$
352	90				
277	25	Ph_2Sb^+			
275	40				
273	19				

TABLE 3

INTENSITIES AND "d-SPACINGS" (Å) DERIVED FROM X-RAY POWDER PHOTOGRAPHS OF PRODUCTS LISTED IN TABLE 2

Reflection line No.	Product B		Product C		Product D		Product E	
	Rel. intensity	d	Rel. intensity	d	Rel. intensity	d	Rel. intensity	d
1	m	5.277	m	5.330	s	8.561	s	8.561
2	s	4.567	s	4.591	s	7.099	s	7.235
3	m	4.374	s	4.410	s	6.448	s	6.371
4	m	4.016	m	4.016	w	5.729	vw	5.985
5	m	3.666	m	3.663	w	5.077	w	5.405
6	m	3.449	m	3.294	s	4.745	vw	5.145
7	w	3.168	w	3.179	m	4.591	vw	4.796
8	m	3.015	m	3.028	s	4.439	s	4.323
9	m	2.619	m	2.622	s	4.318	s	4.095
10	m	2.520	m	2.531	w	3.708	vw	3.940
11	w	2.415	w	2.421	m	3.475	vw	3.739
12	w	2.272	w	2.281	m	3.401	s	3.566
13	w	2.186	w	2.201	w	3.247	m	3.431
14	w	2.129	w	2.135	w	3.168	vw	3.267
15	w	2.082	w	2.097	vw	2.982	vw	3.153
16	m	1.981	m	1.988	w	2.786	vw	3.114
17	vw	1.944	w	1.946			vw	3.021
18	w	1.857	w	1.860			w	2.943
19	w	1.818	w	1.824			w	2.876
20	w	1.772	w	1.781			w	2.778

2.18; Sb, 52.75%). Prolonged mild heating, to about 75°, appears to have caused a stepwise degradation of product A to smaller fragments which are then soluble in carbon tetrachloride.

The solubility tests, as well as the extraction experiment, indicated that a suitable means for recrystallizing the products was not readily available and that indiscriminate heating of the products leads to a mixture of compounds. This latter point was further emphasized when product C was heated under vacuum at approximately 200° for several days. The infrared spectrum of the residue after trituration with ether [Found: C, 51.76; H, 3.61; O, 8.28. $[(C_6H_5)_2Sb(O)]_2O$ (diphenylstibinic anhydride) calcd.: C, 48.05; H, 3.36; O, 8.00%.] was quite different from that of the original material but very similar to the infrared spectrum of the insoluble mixture isolated in the carbon tetrachloride.

The slight solubility of our isolated products (Table 1) in most organic solvents that do not react with the solute species precluded determination of molecular weights. Schultz and McEwen[6] reported a product of triphenylstibine oxide, prepared by heating tetraphenylstibonium hydroxide in xylene, that was sufficiently soluble in boiling benzene so that a molecular weight by osmometry could be determined. A value of 367±3 (theoretical, 369) indicated that a monomeric triphenylstibine oxide (m.p. 221.5–222°) was isolated. The material reported in our work, which was prepared by the heating of tetraphenylstibonium hydroxide in *p*-xylene (Table 1, E), is not the same material as reported by the above authors. Although Briles and McEwen[7] reported that their isolated triphenylstibine oxide was soluble enough in carbon tetrachloride to obtain a PMR spectrum, the low solubility of products A, B, and C was such that a saturated carbon tetrachloride solution did not give PMR spectra which could aid in characterizing the products. An "oxide" sample, kindly supplied by Prof. McEwen (University of Massachusetts), exhibited chemical shifts of 7.29 and 7.68 ppm (centers of multiplex absorption regions measured from TMS in carbon tetrachloride); Briles and McEwen[7] reported 7.28 and 7.59 ppm. The observed chemical shifts of the following compounds are listed for comparison: triphenylstibine, 7.27 ppm; triphenylstibine dichloride, 7.48 and 8.22 ppm; and triphenylstibine dihydroxide, 7.36 and 7.67 ppm.

Free iodine was formed by the reaction of product A or B with a glacial acetic acid solution of potassium iodide. This result could not be taken as absolute proof for the presence of a peroxide group, as suggested by Briles and McEwen[7], because the test was also positive when dimethyl sulfoxide was treated with the iodide solution. A natural consequence of this investigation was an attempt to oxidize triphenylstibine with dimethyl sulfoxide; no reaction occurred under the conditions used. The inference is that triphenylstibine oxide (products A, B and C) is a stronger oxidizing agent than dimethyl sulfoxide. Evidence that products A and B did not contain hydrogen peroxide was found when the infrared regions at 3250, 3150, and 2830 cm^{-1} were observed to be free of absorption; these regions are reported to have characteristic absorption for the hydrogen peroxide adducts of triphenylphosphine oxide[8] and triphenylarsine oxide[9].

In the infrared region between 1600 and 800 cm^{-1}, the absorptions attributed to monosubstituted phenyl groups agreed with the already documented assignments[10–13]. Most infrared spectra were similar in this region and identifying features for a specific compound were limited; consequently, this region will not be considered

TABLE 4

REPORTED Sb–O STRETCHING FREQUENCIES

Compounds	Physical state	Frequencies (cm^{-1})	References
Ph_4SbO–Alkyl	Nujol or Fluorolube mulls	335–320	20
Me_4Sb-Oxinate to $MeSbCl_3$-Oxinate	KBr disk	497–530	21
$(Ph_4Sb)_2O$	KBr disk	660 and 652	22
$(Alkyl)_3SbO$	CCl_4 solution	678–650 and 450	19
Ph_3SbO (monomer)	Nujol mull	680 and 475	6
$(R_3SbOSbR_3)X_2$	Nujol mull	736–790	10, 23, 24
$(R_3SbCl)_2O$	Nujol or Kel-F mull	736–788	25

further. However, the spectral region below 800 cm^{-1} was more distinctive and was found useful in the qualitative identification of the various products. A brief review of the conflicting Sb–O infrared spectral data is given by Doak and Freedman[1].

The infrared and Raman spectra of triphenylarsine and triphenylarsine oxide leave little doubt as to the assignment of the stretching mode of the As=O group to the absorption at 886 cm^{-1}. The absorption is in a region which is not complicated by the absorptions of the phenyl groups. Triphenylarsine oxide labeled with ^{18}O has also been used to confirm this assignment[14]. Therefore, we expected the "Sb=O" group to absorb in the 750 to 650 cm^{-1} region based on (*a*) the As=O assignment, (*b*) the strong infrared absorption reported at 740 cm^{-1} for both Sb_2O_3 and Sb_2O_5[15,16], (*c*) the principal absorptions of cubic (750 cm^{-1}) and orthorhombic (690 cm^{-1}) forms of Sb_2O_3 and of cubic (800 cm^{-1}) and monoclinic (840 cm^{-1}) forms of As_2O_3[17,18], (*d*) the respective differences in mass between Sb and As, and (*e*) the calculated limits of the Sb–O vibrations using Gordy's rule[19]: ν(Sb–O) 550 and ν(Sb=O) 803 cm^{-1}.

A summary of reported Sb–O stretching frequencies is listed in Table 4. For the products listed as triphenylstibine oxide in this work (products A, B, and C in Table 1), the infrared and Raman regions of interest were between 625 and 775 cm^{-1}

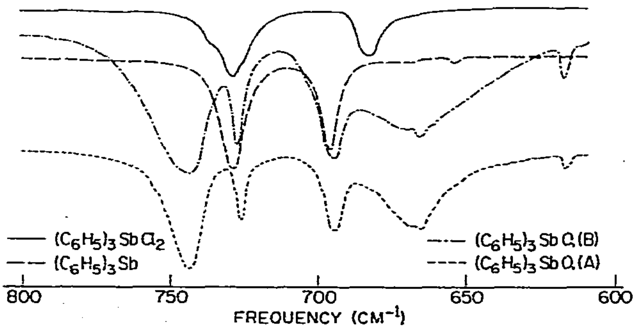

Fig. 1. Infrared spectra of triphenylstibine, triphenylstibine dichloride and triphenylstibine oxide. Expanded scale of 625 to 775 cm^{-1} region.

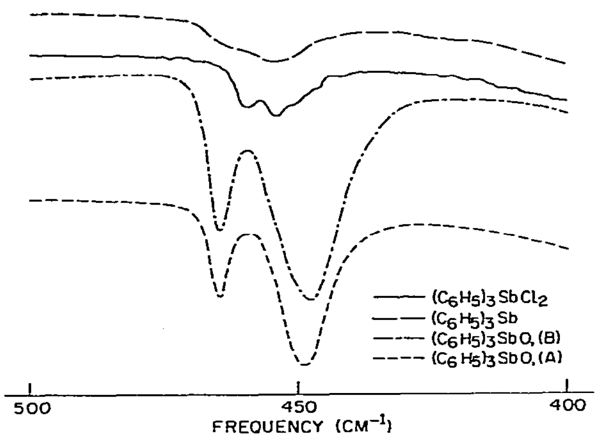

Fig. 2. Infrared spectra of triphenylstibine, triphenylstibine dichloride and triphenylstibine oxide. Expanded scale of 400 to 500 cm^{-1} region.

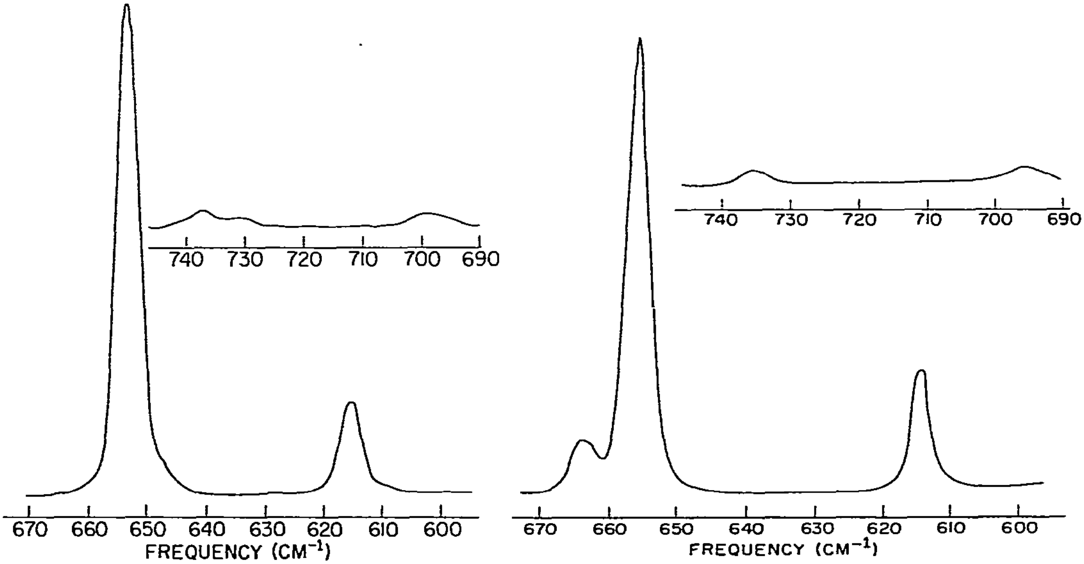

Fig. 3. Raman spectra of triphenylstibine and triphenylstibine oxide: a, triphenylstibine; b, triphenylstibine oxide (product A).

and between 400 and 500 cm^{-1}. Figures 1–3 show expanded scale spectra of the pertinent regions for triphenylstibine and its derivatives. The spectra of products A, B, and C are characterized by the presence of a strong infrared absorption at 744±3 cm^{-1} (Fig. 1) that is absent in the Raman spectra (Fig. 3), and a complex absorption with a broad peak centred at 669±2 cm^{-1} with a sharper absorption superimposed at 665±2 cm^{-1}. The former absorption is not detected in the Raman spectra, but the latter absorption has a Raman component at 664 cm^{-1} and is believed to arise from splitting of ν_2 similar to that found in the triphenylgermanium halide[26] and tetraphenylgermanium[27] systems. Based on the expected region for the Sb–O stretching vibration between 750 and 650 cm^{-1}, the absorption at 744±3 cm^{-1} is assigned to the antisymmetrical stretch of Sb–O–Sb.

The absorptions at 669 cm^{-1}, 75 cm^{-1} lower than the antisymmetrical mode, are assumed to be associated with the Sb–O symmetrical stretching vibration. Because the absorption at 744 cm^{-1} and 669 cm^{-1} are not present in the Raman spectra, we conclude that the nature of the Sb–O bond is quite different from the P=O and As=O bonds in the corresponding $(C_6H_5)_3M–O$ compounds. The Raman-active P–O and As–O vibrations indicate that these bonds must be more covalent than the Raman inactive Sb–O vibrations. This inactivity suggests that the Sb–O structural environment may be similar to that of the polysiloxane backbone $(–SiO–)_x$. Consequently, the Sb–O bond is further characterized when the Raman and infrared spectra[28] of poly(dimethylsiloxane) are compared with the present spectral data for triphenylstibine oxide. Similar features are noted in the spectra. The strong Si–O–Si antisymmetrical stretching vibration seen in the infrared spectrum between 1000 and 1100 cm^{-1} is absent from the Raman spectrum. However, the strong Raman line at about 490 cm^{-1}, attributed to the symmetrical Si–O–Si stretching vibration, is weak in the infrared. The fact that neither antisymmetrical nor symmetrical stretching vibrations attributed to the Sb–O–Sb structure appear to be Raman active is consistent with the predicted more ionic nature of Sb–O than Si–O bonds in a polymer structure.

Wing and Callahan[29] have examined the differences between the antisymmetrical and symmetrical stretching frequencies, $\Delta\nu_{antisym}$, of several oxo-bridged, M–O–M systems of inorganic polymers and make the following suggestions: $\Delta\nu_{antisym}$ 600 to 700 cm^{-1} for linear species, 200 to 400 cm^{-1} for bent species, and 100 cm^{-1} for dioxo-bridged compounds whose infrared spectra generally exhibit three absorptions associated with the M–O bonds. The vibrational frequencies of the bridge systems are strongly sensitive to the M–O–M bond angle; consequently, the angular dependence and number of infrared active modes serve to distinguish between mono- and dioxo-bridged systems. If the assignment ν_{sym} 669 cm^{-1} is accepted, then the relatively small value of $\Delta\nu_{antisym}$ 75 cm^{-1} could not be explained on the basis of a mono- or dioxo-bridged system. However, the metal–oxygen systems studied by Wing and Callahan[29] differ from poly(triphenylstibine oxide); the latter polymer structure could allow interactions between the π-electrons of the oxygens in the polymer backbone and vacant π-orbitals of benzene rings attached to antimony. Consequently, a bent polymer backbone of Sb–O–Sb units, with a shortened Sb–O bond length (similar to the dioxo-bridged systems), is predicted, and the small separation between ν_{anti} and ν_{sym}, without splitting, would be consistent with the observed value.

An alternate explanation could be made if the absorption observed in the 670 cm^{-1} region were due to end-groups of a low (tetramer or pentamer) polymer chain (Sb=O, SbOH, etc.). Then, one could argue that the absorption at 450 cm^{-1} is the b_2, ν'_{19}, mode and somewhat weaker peak at 465 cm^{-1} is due to the symmetrical Sb–O–Sb stretching mode. If the assignments ν_{anti} 744 and ν_{sym} 465 cm^{-1} are assumed correct, then the value of about 280 cm^{-1} for $\Delta\nu_{antisym}$ would correspond to the bent M–O–M bonds described by Wing and Callahan[29]. However, we favor the first interpretation (Table 5) for the following reasons: (1) the infrared intensity of the 669 cm^{-1} band is too great to be due to either end groups or small amounts of impurities, and (2) the ring fundamental ν'_{19} is definitely a multiplet in triphenylstibine[30] and there is little reason to expect that this, or some splitting, would not also arise in the spectrum of triphenylstibine oxide. Furthermore, in an extensive study of phenyl-substituted pentavalent antimony compounds, Doak *et al.*[10] report two bands of medium intensity in the vicinity of 450 cm^{-1}. They assign the absorption band occurring near 454 cm^{-1} to a phenyl ring frequency and the second absorption to the antisymmetric antimony–carbon stretching, which may be above, slightly below, or superimposed on the phenyl frequency[10,25,31]. If the symmetrical Sb–O–Sb stretching mode did occur in the 465 cm^{-1} region, it may be degenerate with one or more phenyl ring modes and not be observed.

TABLE 5

INFRARED AND RAMAN DATA (cm^{-1}) AND PROPOSED ASSIGNMENTS FOR TRIPHENYLSTIBINE AND POLY(TRIPHENYLSTIBINE OXIDE)

A. $(C_6H_5)_3SbO$ (Products A and B)[a]		Assignment	*B.* $(C_6H_5)_3Sb$[a]	
IR	Raman (%)[c]		IR	Raman (%)[c]
744 s[b]		Antisym. Sb–O Stretch		
726 s	737(4)	ν_4, Out-of-plane C–H bend	742 w(sh) 729 s	738(4)
694 s	696(4)	ν_8, Out-of-plane ring deformation	696 s	699(4)
669 s(br)		Sym. Sb–O Stretch		
665 vw(sh)	664(12) 656(100)	ν_2, Ring breathing, mass sensitive a_1 mode	655 w	654(100)
624 w 617 w	615(28)	ν_{18}, In-plane ring deformation		616(18)
464 m 450 s		$\nu_{19'}$, C–H perpendicular bend, mass sensitive b_2 mode	463 458 w(br) 450	465(2) 460(3) 450(1)
	400 vw	ν_{20}, ring deformation		400(2)

[a] Raman and infrared absorptions given to $\pm 3\ \mathrm{cm}^{-1}$. [b] s strong, m medium, w weak, b broad, sh shoulder, v very. [c] Raman intensities given as % of strongest absorption in 800–400 cm^{-1} region.

Comparison of the infrared spectra of products D and E showed a close similarity between the products (note analysis in Table 1), but the infrared spectra were quite different from that of triphenylstibine oxide (products A, B, and C), and suggested a mixture of products. Insight into the nature of the products D and E was gained from two separate attempts to purify samples of tetraphenylstibonium hydroxide. In one experiment the hydroxide was dried for a prolonged period over phosphorus pentoxide under reduced pressure at room temperature and in the other, it was recrystallized from absolute ethanol. In both cases the resulting compound corresponded to bis(tetraphenylstibine) oxide, $(Ph_4Sb)_2O$. A similar dehydration has been noted when the hydroxide is heated to 100° or recrystallized from hot aqueous methanol[1]. The infrared and Raman spectra of the oxide showed a close correspondence to the spectra of D and E. The X-ray powder analyses of all three materials also gave similar results. Products D and E were also compared with $(Ph_3SbCl)_2O$; the results were inconclusive save that the infrared spectrum and X-ray powder photographs of this compound differed from those of compounds D and E and from $(Ph_4Sb)_2O$.

Our inability to isolate single crystals of the products or to label the products with ^{18}O has prevented single crystal X-ray, Raman depolarization and isotopic shift studies to corroborate our spectral assignments. It would also be helpful if deuterated poly(triphenylstibine oxide) were available to resolve the infrared active phenyl modes. Work is continuing on these problems. The spectra in the region 800 through 400 cm^{-1} (Table 5) do, however, provide a ready means of identifying poly(triphenylstibine oxide), a polymeric material which is slightly soluble in most organic solvents.

EXPERIMENTAL

Infrared data were recorded on a Perkin–Elmer Model 457 or a Beckman IR-12 spectrophotometer using Nujol oil mulls (10 mg sample/drop oil) and Raman data from powdered samples were recorded on a Cary Model 81 Raman spectrometer using a helium/neon laser energy source. Calibrations of the spectra were accomplished with carbon dioxide and deuterium cyanide for the infrared instruments, and carbon tetrachloride for the Raman spectrometer. Thin KBr windows were convenient for the regions of interest.

The PMR spectra were recorded on a Varian HA-100 in the field sweep mode using TMS as a lock signal in carbon tetrachloride solutions. Mass spectral data were obtained by directly inserting the solid sample into a heated inlet system of a CEC Model 103C or into the ion source of a Bendix time-of-flight spectrometer via a direct insertion probe. The latter inlet probe system was described recently and the temperatures of the samples were measured to be between 100° and 150° [4]. Triphenylstibine, used to check the inlet system, had sufficient vapor pressure, under the conditions used, so that only minimal heating was necessary for a useful mass spectum. Other compounds were heated until a sufficient quantity of sample was obtained for an intense spectrum. A DuPont 900 differential thermal analyzer was used to record thermal data. X-ray powder analyses were determined with K_α radiation and a nickel filter, and the photographs were recorded on a 19.0 cm diameter camera using a VanArkel film mounting. Intensities were estimated visually. Temperatures reported herein are uncorrected.

Material

The triphenylstibine (Eastman Organic Chemicals) and triphenylstibine dichloride (Eastman Organic Chemicals) were used without further purification. Tetraphenylstibonium hydroxide was prepared according to the method of Affsprung and May[32].

Preparations (Melting points and analyses are given in Table 1)

1. *Reaction between triphenylstibine and hydrogen peroxide.* A sample of triphenylstibine oxide was prepared by a modification of the methods reported by Shriner and Wolf[33] for the preparation of triphenylarsine oxide and used by Goodgame and Cotton[34]. Twelve grams (34 mmoles) of triphenylstibine, m.p. 40°, were dissolved in 20 ml of reagent grade acetone in a 50 ml 3-neck flask fitted with a stirrer, thermometer, and dropping funnel. After the solution was cooled to between 0° and 5°, a solution of 30% hydrogen peroxide (4.5 g, 40 mmoles) in acetone (10 ml) was added dropwise at such a rate that the vigorously stirred reaction mixture could be

maintained at the original temperature with a salt/ice bath. When approximately half of the hydrogen peroxide solution had been added, the reaction mixture became turbid and on further peroxide-solution addition, a finely divided white solid formed. The resulting thick mixture was difficult to stir and 20 ml of acetone was added before the remaining peroxide solution was added. After the peroxide addition was complete, the ice bath was removed and the solution stirred for 45 min at room temperature. Acetone was removed from the solid by transferring the reaction mixture to a 500 ml flask and flash evaporating the solvent from the solid. The white powdery residue began to melt at 277°, turned brown, and at 280°, the yellow melt began to decompose. Sodium-dried benzene (250 ml) was added to the white powder and the mixture was refluxed using a Dean–Stark water trap and a water-cooled condenser; approximately 1 ml of water was collected in the trap. After cooling, filtering, washing with dry benzene and drying the product at 80° over phosphorus(V) oxide at reduced pressure for 25 h, a white powder (10 g, 80% yield) was isolated. The solid melted sharply at 280° to a milky melt which became clear at 300° with some evidence of decomposition.

2. *Hydrolysis of triphenylstibine dichloride and dibromide.* Triphenylstibine dichloride (5 g, 11.8 mmoles) was dissolved in acetone and ethanolic potassium hydroxide (0.2 *M*) was added until the solution was alkaline as determined by a pH meter. Then the solution was warmed for an hour (30°) and concentrated by evaporating some of the solvent. On the addition of water, a white precipitate formed and was filtered, washed with water, and oven-dried at 150° until no hydroxyl bands could be detected in the infrared spectrum. The same procedure was used for the hydrolysis of triphenylstibine dibromide.

3. *Thermal decomposition of tetraphenylstibonium hydroxide.* Briles and McEwen[7] reported that tetraphenylstibonium hydroxide undergoes decomposition in xylene solution at 70–80° to produce benzene and triphenylstibine oxide in 90% yield. One product that we studied was prepared in this manner and kindly supplied by Prof. McEwen. A second sample, starting with tetraphenylstibonium hydroxide, was obtained by heating the hydroxide in *p*-xylene under an atmosphere of N_2 at 60–70° for seven days.

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