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THE SYNTHESIS AND INFRARED SPECTRA OF SOME GROUP Va CHALCOGENIDES*

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SUMMARY

The trialkylstibine oxides, a poorly understood group of compounds, have now been unequivocally characterized. The fundamental stretching frequencies ν(Sb=O), ν(Sb=S), ν(Sb=Se) and ν(P=Te) have been assigned in a series of compounds, $R_3M{=}X$ where M is a P or Sb atom and X is O, S or Se.

INTRODUCTION

Studies which have been concerned with the synthesis and physical properties, especially the spectral properties, of chalcogenides having the general formula R_3MX, where R represents an alkyl or aryl group, M a Group Va atom, and X a Group VIa element, have been actively carried on in this laboratory during the past several years. The preparation of these compounds and studies of their infrared spectra, especially as these concern the fundamental stretching frequencies of the respective M=X bonds, have been reported for the following compounds: R_3PO[1], R_3PS[2,3] and R_3PSe[2,3], R_3AsO[4], R_3AsS[5] and R_3AsSe[6]. In addition, the preparation of compounds of the general formula R_3SbS[7], R_3SbSe[7], and R_3PTe[8] have also been reported, although the infrared stretching frequencies of the M=X bonds in these molecules have not been previously measured.

In order to extend the study of the series, the present work reports on the preparation and measurement of the fundamental stretching frequencies, ν(M=X) associated with M=X bonds of the trialkylstibine oxides, trialkylstibine sulfides, trialkylstibine selenides and trialkylphosphine tellurides.

RESULTS AND DISCUSSION

During the course of this work nineteen compounds of the general formula $R_3M{=}X$ were synthesized. While some of these have been reported earlier in the literature[7-10], not all of them have been properly characterized. The trialkylstibine oxides are a case in point. Dyke and Jones[10] described the tripropyl-, tributyl-, and tripentylstibine oxides as "gelatinous substances", and did not report any physical constants. Their failure to obtain solid crystalline materials can be attributed to two

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factors. First, they carried out their reactions in absolute ethyl alcohol. In this solvent the oxidation reaction occurs extremely rapidly, and, as has been observed in this study, there occurs a secondary reaction between triethylstibine oxide and ethanol to give triethyldiethoxyantimony, $(C_2H_5)_3Sb(OC_2H_5)_2$. The following reaction therefore takes place to a considerable extent:

$$(C_2H_5)_3SbO + 2\,C_2H_5OH \rightarrow (C_2H_5)_3Sb(OC_2H_5)_2 + H_2O$$

Although this reaction has been observed to occur to a lesser degree in the case of the higher trialkylstibine oxides, it would, nevertheless, contaminate the final products. Secondly, the handling of the trialkylstibine oxides is impossible under ordinary atmospheric conditions. Their exceedingly high sensitivity to moisture makes it absolutely essential that all manipulations are performed in a rigorously moisture free environment.

The trialkylstibine oxides have now been unequivocally characterized as colorless, crystalline solids. Trimethylantimony oxide has been handled in pure form by several workers[11-13], the existence of triphenylstibine oxide has also been well documented[14,32]. There is no reference in the literature concerning the existence of triethylstibine oxide other than the early work of Löwig and Schweizer[9] and Löwig[15].

Improved methods have also been devised for the synthesis of trialkylstibine sulfides and selenides and the trialkylphosphine tellurides. Thus, tripentylstibine sulfide and selenide and tricyclohexylstibine selenide were prepared for the first time. The yields of the trialkylphosphines were substantially increased from the 10–20% range reported earlier[8,16] to 75–80%. The failure to obtain the tripentylphosphine telluride and trioctylphosphine telluride as pure compounds, is attributed to the instability of these molecules.

The location of the $\nu(M{=}X)$ stretching vibrations

The region of the $\nu(M{=}X)$ vibration was located by comparison of the spectrum of the R_3MX compound with that of the parent R_3M compound or by comparison of pairs of R_3MX compounds having different X substituents. It is admittedly an approximation to consider the normal vibrations of the R_3MX molecule as characteristic group vibrations, since the energy of a normal vibration will not be entirely localized in a given bond. Nevertheless, the greater part of the energy will be highly localized, and in this sense, the term "characteristic group vibration" may be used. Since the vibrational frequencies of most R–M bands are found at nearly the same positions in the spectra of R_3MX, R_3MY and R_3M series of compounds, this assumption is further justified. When a band appears in the R_3MX spectrum, but is absent in the R_3MY spectrum, while the R–M bands remain essentially at the same positions, it is quite correct to conclude that the new band arises from an M–X vibration, although, strictly speaking, this may not be rigorously justified[17-19].

The region of the fundamental $\nu(M{=}X)$ stretching vibration was scanned on an expanded scale and at very slow speed in order to locate the frequency of maximum absorption. The region of interest in such a spectrum is shown in Fig. 1. The values of the fundamental $\nu(M{=}X)$ vibrations ($\pm 2\ cm^{-1}$) of the compounds studied are listed in Table 1.

By means of Gordy's empirical equation[20] the force constant of an isolated

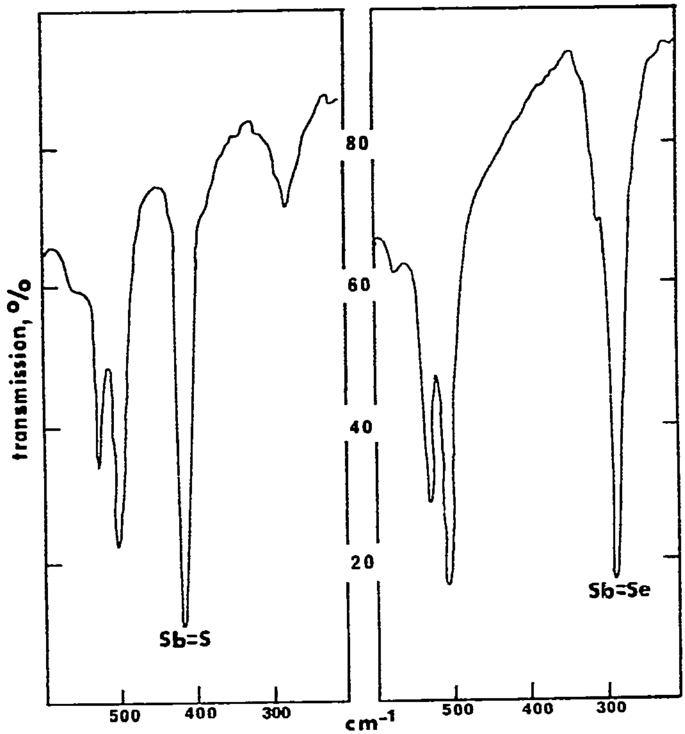


Fig. 1. (a) Infrared spectrum of triethylstibine sulfide (Nujol mull, polyethylene cells) and (b) of triethylstibine selenide (Nujol mull, polyethylene cells) in the region 200–700 cm^{-1}.

TABLE 1

THE FUNDAMENTAL ν(M=X) STRETCHING VIBRATIONS (cm^{-1}) OF R_3M=X COMPOUNDS

R	Physical state	ν(Sb=O)	ν(Sb=S)	ν(Sb=Se)	ν(P=Te)
C_2H_5	CCl_4 solution	678, 478	439		
	Solid KBr pellet		422	272	
n-C_3H_7	CCl_4 solution	650, 450	439		
	Pure liquid		434	300	
	Solid KBr pellet				400, 445
n-C_4H_9	CCl_4 solution	650, 450	440		
	Pure liquid		434	294	
	Solid KBr pellet				400, 462
n-C_5H_{11}	CCl_4 solution		438		
	Pure liquid	650, 450	434	296	405, 467
cyclo-C_6H_{11}	CCl_4 solution		435, 440		
	Solid KBr pellet		435, 440	290	518
n-C_8H_{17}	Pure liquid				405, 455

M–X vibration can be estimated. This value, when substituted into the fundamental equation for a harmonic oscillator (1), which relates the frequency to the values of the force constant k and the reduced mass μ of the M and X atoms, gives the approximate value of the frequency of an isolated M–X vibration.

$$\nu(\text{cm}^{-1}) = 1307(k/\mu)^{\frac{1}{2}} \qquad (1)$$

Values thus calculated are for the isolated vibration of the two atoms M and X, and set only upper and lower limits for the frequency of this vibration in the case of a double and single bond, respectively. In fact, no vibration is totally isolated, but depends upon the masses and chemical structure of the substituent groups. This vibration then should be expected to occur between the two limits.

The upper and lower limits for the Sb–O, Sb–S, Sb–Se and P–Te vibrations have been calculated by substituting into Gordy's formula the necessary quantities from Pauling[21], and are listed in Table 2.

TABLE 2

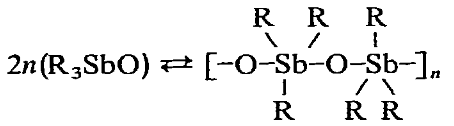
CALCULATED LIMITS OF THE M–X VIBRATIONS USING GORDY'S RULE

M–X	ν(M–X) ν for single bond (cm⁻¹)	ν(M=X) ν for double bond (cm⁻¹)
Sb–O	550	803
Sb–S	338	485
Sb–Se	234	333
P–Te	330	473

The fact that for most of the R_3MX compounds studied, the assigned frequencies appear within these limits imparts a greater degree of confidence to these assignments. However, the assigned frequency for the tricyclohexylphosphine telluride and the lower frequency components of the trialkylstibine oxides do not fall within the calculated limits.

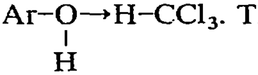
The spectra of the trialkylstibine oxides were examined in carbon tetrachloride solution using cesium bromide cells. In each case two absorption maxima were observed, the higher frequency component having the greater intensity. These two frequencies occur at 450 cm^{-1} and 650 cm^{-1} for tripropyl-, tributyl- and tripentylstibine oxides and at 478 cm^{-1} and 678 cm^{-1} for triethylstibine oxide. In addition, the spectrum of tripentylstibine oxide, in the pure liquid state, was measured between cesium iodide plates. Comparison with the solution spectrum showed no frequency shift of the two absorption bands.

A possible explanation for the appearance of the doublets with such a great separation could be attributed to molecular association, *i.e.*:



$$2n(R_3SbO) \rightleftarrows [\text{–O–}\underset{R}{\overset{R}{Sb}}\text{–O–}\underset{R\ R}{\overset{R\ R}{Sb}}\text{–}]_n$$

However, equilibrium among various associated species, including cyclic species $(\text{–}SbR_3\text{–}O\text{–})_3$ is possible. The band at the lower frequency could then be assigned to the Sb–O configuration. Recently Doak, Long and Freedman[22] suggested the range of 335 cm^{-1} to 320 cm^{-1} for the Sb–O stretching frequency. However, Meinema and co-workers[23] have reported that the Sb–O stretching frequency occurs at 497–530 cm^{-1} in a series of oxinates. This is in reasonable agreement with the lower frequency value observed in this work. The differences can be attributed to differences in the symmetry classes as well as to chemical differences, *i.e.*, the oxygen atom in the stibine oxides is not covalently bound to a second atom. Thus, coupling effects of the type encountered in the oxinates are not present in the case of the alkylstibine oxides.

It is not surprising that the triethyl derivative is monomeric in chloroform. Zingaro and Coleman[33], on the basis of measurements of the dielectric constants, found that the intermolecular association of 4-sec-butyl-2-(α-methylbenzyl)phenol is inhibited in chloroform due to the acceptor action of chloroform molecules, *i.e.*,  $\mathrm{Ar{-}\underset{\underset{H}{|}}{O}{\rightarrow}H{-}CCl_3}$. The ability of chloroform to function as a Lewis acid has been discussed also by Pimentel and McClellan[34]. The fact that $Et_3Sb{=}O$ is monomeric in this solvent suggests association of the type, $Et_3Sb{-}\underset{..}{\ddot{O}}{:}\rightarrow H{-}CCl_3$. This would indicate that $Et_3Sb{=}O$ is a rather strong donor. Finally, McEwen and coworkers[32] have found that $Ph_3Sb{=}O$ is monomeric at the boiling point of benzene.

Jensen and Nielsen[24] were unable to identify any absorption due to the Sb=O group in the case of the triphenylstibine oxide, and for this reason they attribute a pseudoionic character to the triphenylstibine oxide. Supporting evidence for the pseudoionic character of triphenylstibine oxide is its high melting point and its insolubility in organic solvents. These workers observed, however, a very strong band at 692 cm^{-1} and a medium intensity, broad band at 458 cm^{-1} which they attributed to phenyl ring vibrations. It seems possible that the Sb=O vibration is not absent, but is masked by phenyl ring vibrations. For the triphenyl derivative, the Sb=O vibration should be at a frequency higher than that of the trialkyl derivatives. The greater electron-withdrawing character of the phenyl groups will increase th Sb–O order and the frequency will rise as has been observed with other aromatic substituents of the Group Va chalcogenides[2–5]. Moreover, Briles and McEwen[32] reported that Ph_3SbO shows absorption peaks at 680 and 475 cm^{-1}, in agreement with observations herein reported for the trialkyl derivatives.

For the trialkylstibine sulfides the fundamental vibration, ν(Sb=S), occurs as a singlet in every case but one. The exception is that of tricyclohexylstibine sulfide, where it is observed as doublet in solution, with a band separation of 5 cm^{-1}. There is a small shift to a slightly higher frequency in the location of this vibration for the dissolved compounds as compared with that in the pure state. In the triethylstibine sulfide this absorption is shifted from 422 cm^{-1} in the solid state to 440 cm^{-1} in solution. The other trialkylstibine sulfides show a shift to the latter value from 434 cm^{-1} in the liquid state.

The triethylstibine selenide was examined in a KBr pellet and as a Nujol mull. No doublets were observed, but the mull sample was partially decomposed. Because the trialkylstibine selenides might decompose in solution, they were examined only in the absence of solvents. Under these conditions ν(Sb=Se) was always observed as a singlet.

The trialkylphosphine tellurides, with the exception of the tricyclohexylphosphine telluride, exhibited two absorption bands in the 400–470 cm^{-1} region. The lower frequency component at *ca.* 400 cm^{-1} appeared to remain constant for all the compounds studied. The band at the higher frequency, however, varied with the alkyl substituent. The band separations vary from 45 cm^{-1} for the tripropylphosphine telluride to 62 cm^{-1} for the tributyl and tripentyl derivatives, while the trioctylphosphine telluride exhibited a difference of 50 cm^{-1}.

The separation and location of the P–Te doublets remained the same when the solid materials were examined as Nujol mulls. A study of these spectra in solution as a function of temperature was not possible because of ready thermal decomposition of the compounds. One possible explanation for the observed doublets would be the existence of stable modified tetrahedral configurations of the molecules, similar to the explanation suggested by Bell *et al.*[25] for the occurrence of phosphoryl doublets in the spectra of triaromatic phosphates. Another possible explanation is that the absorption at the lower frequency is part of the P=Te vibration. This can be substantiated from the fact that most ν(M=X) vibrations remain more or less constant with the variation of the alkyl substituents. If this is the case, then the absorption at the higher frequency can be attributed to the Fermi resonance interaction of the overtone of a degenerate mode of the alkyl group, $\rho_r(MR_3)$, with the M=X stretching vibration. In the spectra of trimethyl phosphite[26] and trimethyl phosphate[27] the antisymmetric $P(-O-)_3$ bending vibrations have been reported at 225 cm^{-1} and 239 cm^{-1}, respectively. If the corresponding modes for the case of the R_3MX molecules occur close to these values, their first overtones will be close to the higher frequencies observed for the trialkylphosphine tellurides.

Still another possibility is that a once weak unobservable δ_s (RPR) mode increased its intensity due to substitution to become observable. Further insight as to the nature of doublets could be obtained from observation of the Raman spectra. If the absorption at the higher frequency is a fundamental bending mode, dependent on the alkyl group, then according to theoretical expectations it should be depolarized, while the lower symmetric vibration should be polarized.

EXPERIMENTAL

General

The infrared spectra of the trialkylstibine oxides, trialkylstibine sulfides, trialkylstibine selenides and trialkylphosphine tellurides were recorded on a Beckman Model IR-12 double beam spectrophotometer using potassium bromide pellets, Nujol mulls, thin films of the liquids between cesium iodide, potassium bromide or polyethylene plates, or in carbon tetrachloride solution using cesium bromide or iodide cells, as the case required. The spectra were recorded in the 4000–200 cm^{-1} region.

Elemental analyses and molecular weight determinations were performed by the Galbraith Laboratories, Inc., Knoxville, Tennessee.

The melting points and boiling points reported in this study are uncorrected.

The triethyl-, tripropyl-, tributyl- and tripentylstibines were prepared and purified according to the method of Dyke *et al.*[28]. The tricyclohexylstibine was prepared by the method of Issleib and Hamann[29].

The tripropyl- and tripentylphosphines were prepared by the method of Davies *et al.*[30]. The tricyclohexylphosphine was prepared by the method of Issleib and

Brack[31]. The tributylphosphine and trioctylphosphine were purchased from the Aldrich Chemical Company.

Preparations

Trialkylstibine or -phosphine derivatives of chalcogenides have been previously prepared by refluxing the stibine or phosphine with sulfur, selenium or tellurium in an inert solvent[7,8,16], and in the case of trialkylstibine oxides oxidation with mercuric oxide in alcohol[10]. These methods produce undesirable by-products, the purification is difficult and low yields are obtained. For these reasons modified procedures have been devised for the preparation of these compounds in the present work.

In general the reactants were shaken together for a period of a week in the absence of any solvent, heat or light, whenever this was possible. Dry ether was used as the solvent for the preparation of the trialkylstibine oxides and the tricyclohexylstibine selenide without heating. The trialkylphosphine tellurides were prepared by heating the reactants in the absence of any solvent for 2–3 h. An inert atmosphere was maintained throughout all of the manipulations. Exclusion of moisture is essential since the trialkylstibine oxides are extremely hygroscopic. Purifications were effected by freezing out the liquid or solid products at Dry Ice/acetone temperature from ether or petroleum ether. The reactions are quantitative and yields of 70–90% are realized after purification. The physical constants of the compounds prepared in this method

TABLE 3

ANALYTICAL AND PHYSICAL DATA OF SOME TRIALKYLSTIBINE CHALCOGENIDES

Compound	M.p. (°C) or b.p. (°C/mm)	Mol. wt. found[a] (calcd.)	n_D^{25}	Analyses, found (calcd.) (%)		
				C	H	Sb
$(C_2H_5)_3SbO$	144–146	242[b] (224)		32.29 (32.03)	6.50 (6.72)	54.49 (54.12)
$(C_3H_7)_3SbO$	168–170	609 (267)		40.10 (40.48)	8.15 (7.92)	45.36 (45.59)
$(C_4H_9)_3SbO$	177–179	730 (309)		46.80 (46.63)	8.78 (8.80)	39.50 (39.50)
$(C_5H_{11})_3SbO$	109–110/1.5	835 (351)	1.4968	51.04 (51.30)	9.34 (9.47)	34.82 (34.66)
$(C_5H_{11})_3SbS$			1.5325	48.90 (49.06)	9.16 (9.06)	32.91[c] (33.15)
$(C_5H_{11})_3SbSe$			1.5455	43.68 (43.50)	8.20 (8.03)	29.55[d] (29.39)
$(C_6H_{11})_3SbSe$	121–122			48.96 (48.02)	7.77 (7.38)	
$(C_2H_5)_3Sb(OC_2H_5)_2$	70/1.5		1.3928	39.81 (40.16)	8.45 (8.42)	

[a] Molecular masses were determined by vapor pressure osmometry in CCl_4. [b] In $CHCl_3$. [c] S found 8.42, calcd. 8.73%. [d] Se found 18.79, calcd. 19.06%.

were in agreement with those previously reported. Analytical and physical data for the new compounds are listed in Table 3. Representative preparations are described below.

Triethylstibine oxide. Into a 150 ml round bottom flask were placed 16.3 g (0.075 mole) of mercuric oxide and 25 ml of dry ether. The flask was purged thoroughly with nitrogen and then 10.45 g (0.05 mole) of freshly distilled triethylstibine was added dropwise while the contents were stirred by means of a magnetic stirrer. After the addition of the triethylstibine, the flask was stoppered and left on a shaking machine for a week. Magnesium sulfate was added to the mixture and the ether solution was filtered in a closed system to avoid contamination by moisture. The ether was completely evaporated on a water bath under reduced pressure, and white, very hygroscopic crystals remained on the bottom of the evaporating flask. These were subsequently dried over phosphorus pentoxide in a desiccator at reduced pressure. The product could not be sublimed under vacuum, since it was found to decompose easily.

Similar procedures were used for the preparation of tripropyl-, tributyl- and tripentylstibine oxides. It was possible to distill the crude tripentylstibine oxide at a pressure of 1.5 mm and a temperature of 109–110°. The distillation was accompanied by some decomposition which produced low boiling fractions.

Tripentylstibine sulfide. Into a 50 ml round bottom flask were placed 1.76 g (0.055 mole) of sulfur and then, under an atmosphere of nitrogen, were introduced 16.75 g (0.05 mole) of freshly distilled tripentylstibine. The flask was stoppered and it was shaken for a week in the dark. At the end of this period the excess sulfur was removed by filtration. The crude, yellow liquid, tripentylstibine sulfide, was mixed with 25 ml of dry ether and placed in an ice-water bath. The excess of dissolved sulfur crystallized and it was removed by filtration. The clear solution was then placed in a Dry Ice/acetone bath where it remained until most of the liquid had crystallized. The supernatant liquid was poured off and after the addition of 10 ml of ether, the crystallization process was repeated. The ethereal solution was dried over magnesium sulfate and the ether was removed by distillation.

Similar procedures were used for all the trialkylstibine sulfides and selenides with the exception of tricyclohexylstibine selenide, in which case ether was used as the solvent for the reaction.

Tripropylphosphine telluride. Into a 50 ml two neck, round bottom flask, equipped with magnetic stirrer, thermometer and reflux condenser, were placed 32 g (0.20 mole) of tripropylphosphine and 27.7 g (0.22 mole) of tellurium powder. The system was purged thoroughly with nitrogen and the nitrogen atmosphere was maintained throughout the reaction period. The reaction mixture was brought to 100°. Stirring was continued for 3 h at this temperature. The semi-solid mass was cooled and dissolved in 50 ml of petroleum ether (boiling range 69–79°). Then the excess tellurium was filtered off. The petroleum ether solution was placed in a Dry Ice/acetone bath and the tripropylphosphine telluride precipitated out as a yellow crystalline solid. The yellow crystals were removed by filtration and were recrystallized twice in this manner from 50 ml portions of petroleum ether. The crystals were dried in a desiccator over calcium chloride under vacuum. The yield was 80% and a melting point of 45–46° was observed, which is in good agreement with that of 41–42° previously reported[16].

Similar procedures were used for the preparation of tributyl-, tripentyl-, tricyclohexyl- and trioctylphosphine telluride. The crude liquids resulting from the reactions of triamylphosphine and trioctylphosphine with tellurium could not be recrystallized because they decompose in petroleum ether solution by light or on contact with the walls of the container. However, it was possible to obtain the infrared spectra of the impure liquids.

Attempted preparation of triethylstibine oxide by the method of Dyke et al.[10]. Into a 150 ml round bottom flask were placed 16.3 g (0.075 mole) of mercuric oxide and 25 ml of absolute ethyl alcohol. The flask was purged thoroughly with nitrogen. Then, 10.45 g (0.05 mole) of freshly distilled triethylstibine was added dropwise while the contents were stirred by means of a magnetic stirrer. A vigorous exothermic reaction took place with the reduction of mercuric oxide to mercury. Magnesium sulfate was added to the mixture and the alcoholic solution was filtered into a closed system to avoid contamination by moisture. The alcohol was removed *in vacuo* and the resulting liquid was dried over phosphorus pentoxide under reduced pressure. Even after prolonged drying the liquid did not crystallize. It was then distilled under reduced pressure, b.p. 70° at 1.5 mm. This material (Table 3) is probably triethyldiethoxystibine.

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