

THE INFRARED STUDY OF TRIMETHYLANTIMONY(V) DERIVATIVES CONTAINING Sb-O BONDS

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The structures of antimony(V) compounds containing alkyl or aryl groups have not yet been clearly established. In the case of $(\text{CH}_3)_3\text{SbX}_2$ ($\text{X} = \text{Cl}, \text{Br}$ or I), Wells¹ showed on the basis of the X-ray diffraction that these compounds have a trigonal bipyramidal configuration with the C_3Sb group forming the trigonal plane and with the halogens at the apices. However, the Sb-X bond length was somewhat greater than the sum of the covalent radii of Sb and X atoms. Hence he could not conclude with certainty that the halogen atoms were covalently bound.

On the basis of X-ray diffraction studies, Polynova *et al.*² concluded that $(\text{C}_6\text{H}_5)_3\text{SbCl}_2$ also had a trigonal bipyramidal structure. Dipole moment measurement of $(\text{C}_6\text{H}_5)_3\text{SbCl}_2$ ³ indicated that the molecule was symmetrical and that the halogen atoms were covalently bound to the antimony. Also conductivity measurements of $(\text{C}_6\text{H}_5)_3\text{SbCl}_2$ in acetonitrile⁴ gave no evidence of chloride ion. These results suggest that the Sb-Cl bonds in $(\text{C}_6\text{H}_5)_3\text{SbCl}_2$ are predominantly covalent. On the other hand, on the basis of the infrared spectroscopic investigations Long *et al.*⁵ conclude that, in the solid state, trimethylantimony dinitrate, and oxybis(trimethylantimony) derivatives are ionic compounds, and that in triphenylantimony dinitrate the nitrate group is considerably more covalent than in trimethylantimony dinitrate⁶.

To further elucidate the character of the Sb-O bond in trimethylantimony(V) compounds, we are reporting on the preparation, properties and the infrared studies of the following series of compounds; $(\text{CH}_3)_4\text{SbX}$ ($\text{X} = \text{I}$ or NO_3), $(\text{CH}_3)_3\text{SbX}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{OCOH}, \text{OCOCH}_3, \text{OCOC}_2\text{H}_5, \text{OCOC}_3\text{H}_7, \text{OCOC}_6\text{H}_5$ or NO_3) and $\text{X}(\text{CH}_3)_3\text{-SbOSb}(\text{CH}_3)_3\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$ or NO_3).

EXPERIMENTAL

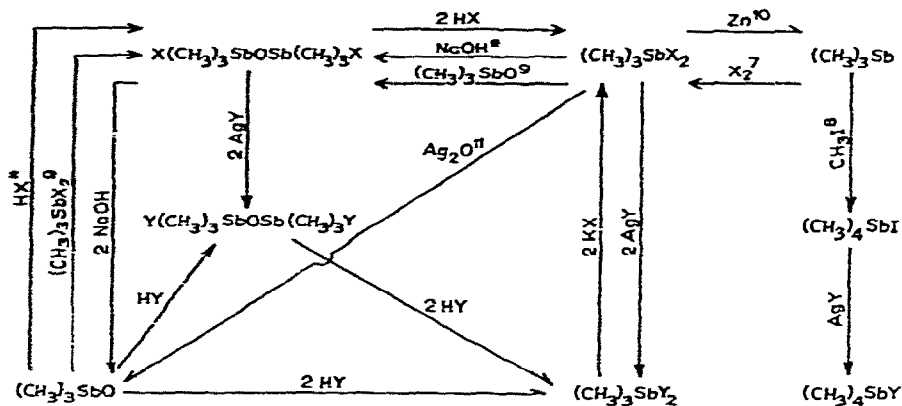
Preparation of starting materials

$(\text{CH}_3)_3\text{SbX}_2$ ($\text{X} = \text{Cl}$ or Br), $(\text{CH}_3)_3\text{SbO}^*$, $\text{X}(\text{CH}_3)_3\text{SbOSb}(\text{CH}_3)_3\text{X}$ ($\text{X} = \text{Cl}$ or Br), and $(\text{CH}_3)_4\text{SbI}$ were prepared by the methods indicated in the reaction scheme (next page).

Trimethylantimony dicarboxylates

$(\text{CH}_3)_3\text{Sb}(\text{OCOH})_2$ and $(\text{CH}_3)_3\text{Sb}(\text{OCOCH}_3)_2$. To 3 g of trimethylantimony oxide 10 ml of formic acid was added. Then the reaction immediately proceeded exothermic-

* Elementary analysis indicated that the material referred to as $(\text{CH}_3)_3\text{SbO}$ is either $(\text{CH}_3)_3\text{Sb}(\text{OH})_2$ or $(\text{CH}_3)_3\text{SbO} \cdot \text{H}_2\text{O}$. However, since the exact formula has not yet been established, for convenience, the formula $(\text{CH}_3)_3\text{SbO}$ will be used in this paper.



Reaction scheme of trimethylantimony (V) derivatives
 $X = \text{Cl}$ or Br ; $Y = \text{NO}_2$ or OCOR

* Although the intermediate compound such as the type of $(\text{CH}_3)_3\text{Sb}(\text{OH})\text{X}$ was previously reported by Friedländer¹² and Morgan *et al.*¹³, we could obtain only its condensation product, $\text{X}(\text{CH}_3)_3\text{SbOSb}(\text{CH}_3)_3\text{X}$.

ally to give a clear solution. The excess formic acid was distilled off under reduced pressure. The white solid obtained was recrystallized from ligroin to give colorless scale-like crystals almost quantitatively; m.p. 81° . (Found: C, 23.18; H, 4.23. $\text{C}_5\text{H}_{11}\text{O}_4\text{Sb}$ calcd.: C, 23.38; H, 4.32 %.) Mol. wt. found cryoscopically in C_6H_6 , 258, 257, 257, at concentrations 0.96, 1.60 and 1.89 % w(sample)/W(solvent) respectively; calcd. for monomer, 257.

Trimethylantimony diacetate was prepared in the same way; m.p. $80.5\text{--}81^\circ$. (Found: C, 29.69; H, 5.21. $\text{C}_7\text{H}_{15}\text{O}_4\text{Sb}$ calcd.: C, 29.51; H, 5.31 %.) Mol. wt. found cryoscopically in C_6H_6 , 285, 293, 279, at concentrations 0.76, 1.15 and 1.71 % w(sample)/W(solvent) respectively; calcd. for monomer, 285.

$(\text{CH}_3)_3\text{Sb}(\text{OCOC}_2\text{H}_5)_2$ and $(\text{CH}_3)_3\text{Sb}(\text{OCOC}_3\text{H}_7)_2$. Trimethylantimony oxide (3 g) was dissolved in 10 ml of propionic acid. Then the excess propionic acid was distilled off under reduced pressure, followed by fractional distillation. A colorless slightly viscous liquid, trimethylantimony dipropionate, was obtained without decomposition; b.p. $110^\circ/6$ mm, n_D^{25} 1.4795. (Found: C, 34.25; H, 6.36. $\text{C}_9\text{H}_{19}\text{O}_4\text{Sb}$ calcd.: C, 34.53; H, 6.13 %.)

By a similar method, trimethylantimony dibutyrate was prepared; b.p. $128^\circ/2.5\text{--}3$ mm. (Found: C, 38.83; H, 6.63. $\text{C}_{11}\text{H}_{23}\text{O}_4\text{Sb}$ calcd.: C, 38.73; H, 6.81 %.)

$(\text{CH}_3)_3\text{Sb}(\text{OCOC}_6\text{H}_5)_2$. An equivalent amount of benzoic acid was added to trimethylantimony oxide in benzene. When the mixture was heated, a clear solution was obtained. After cooling this solution, colorless crystals were obtained. The product was purified by recrystallization from benzene; m.p. 154° . (Found: C, 50.43; H, 4.93. $\text{C}_{17}\text{H}_{19}\text{O}_4\text{Sb}$ calcd.: C, 49.90; H, 4.69 %.) All of these dicarboxylates were soluble in most common organic solvents.

Nitrates

Tetramethylstibonium nitrate, $(\text{CH}_3)_4\text{SbNO}_3$. Tetramethylstibonium iodide (3.2 g) was dissolved in moist acetone, and silver nitrate (1.8 g) in moist acetone was added

to this solution. After heating about one hour on a water bath, precipitated silver iodide was filtered off. Then the filtrate was evaporated to give a white solid. Recrystallization from moist acetone gave colorless crystals; m.p. $> 260^\circ$. (Found: C, 20.00; H, 4.97; N, 5.57. $C_4H_{12}NO_3Sb$ calcd.: C, 19.70; H, 4.96; N, 5.74%.)

Trimethylantimony dinitrate, $(CH_3)_3Sb(NO_3)_2$. To 2 g (0.011 mole) of trimethylantimony oxide 1.2 ml (0.022 mole) of 60% nitric acid was added in 20 ml acetone. A clear solution was obtained immediately. After removal of acetone, the solid obtained was recrystallized from methanol to give colorless crystals; m.p. 140° . (Found: C, 12.55; H, 3.18; N, 9.49; $C_3H_9N_2O_6Sb$ calcd.: C, 12.39; H, 3.12; N, 9.63%.) Mol. wt. found cryoscopically in C_6H_6 , 263 at concentration 1.31% w(sample)/W(solvent); calcd. for monomer, 291. This compound reacts easily with KBr to give trimethylantimony dibromide and potassium nitrate in water as shown in the reaction scheme. For example, trimethylantimony dinitrate (3 g) was dissolved in water, and potassium bromide (3 g) in water was added to this solution. Then the mixture was heated on a water bath for about ten minutes. Colorless crystals, trimethylantimony dibromide, were obtained; m.p. 198° (decomp.).

Oxybis(trimethylantimony) dinitrate, $[(CH_3)_3(NO_3)Sb]_2O$. Addition of 0.6 ml (0.011 mole) of 60% nitric acid to 2 g (0.011 mole) of trimethylantimony oxide in moist acetone gave a clear solution. After removal of the solvent, a white solid was obtained. It was recrystallized from acetone containing a small amount of water. This compound decomposes at 267° . (Found: C, 15.55; H, 3.85; N, 6.15. $C_6H_{18}N_2O_7Sb_2$ calcd.: C, 15.21; H, 3.83; N, 5.91%.) Of these nitrates, tetramethylstibonium nitrate is insoluble in common organic solvents but the other two compounds are soluble or slightly soluble in common polar organic solvents.

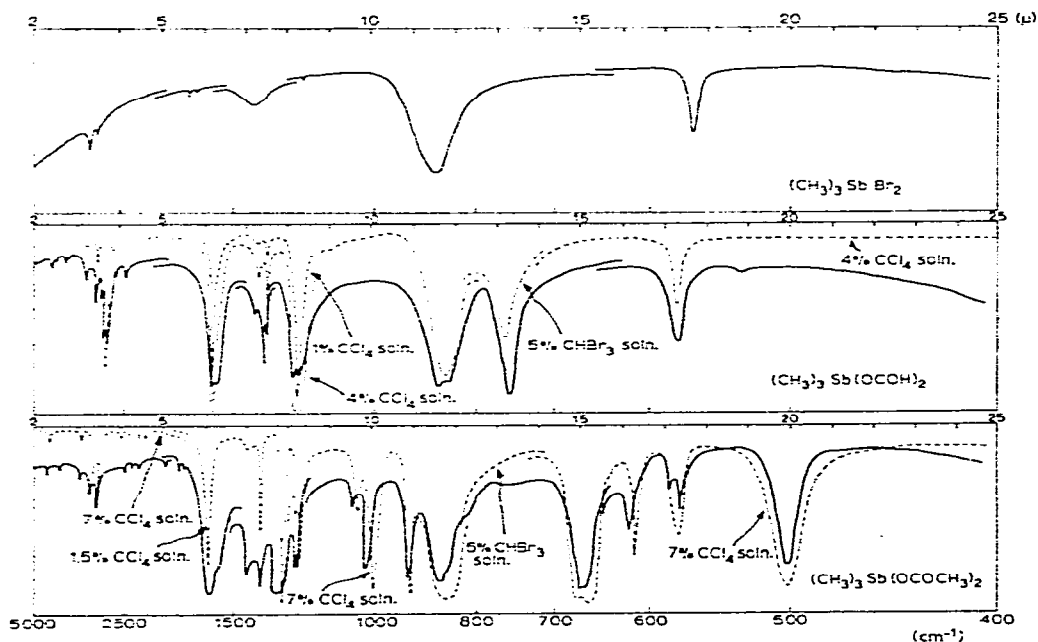


Fig. 1. IR spectra of $(CH_3)_3Sb(OCOR)_2$ and $(CH_3)_3SbBr_2$ — mulls in nujol or HCB; ···· solution in CCl_4 or $CHBr_3$.

Infrared spectra

The infrared spectra from 4000 to 400 cm^{-1} were recorded using a Hitachi EPI-2G spectrophotometer equipped with gratings. The spectra in the solid state were determined as mulls in nujol or hexachlorobutadiene (HCB) using KBr or TlI plates. Spectra of liquid compounds such as trimethylantimony dipropionate or dibutyrate were obtained as liquid films. The spectra in solution were measured in carbon tetrachloride, chloroform or bromoform.

In obtaining the spectra of the nitrates, TlI plates were used because the nitrates readily reacted with the KBr plates according to the reaction described above. This reaction also takes place in KBr disks, therefore the spectra of trimethylantimony dinitrate in KBr were different from those of the nujol mulls. In the KBr disks the band at about 1350 cm^{-1} due to potassium nitrate¹⁴ was observed while the band at 1527 and 1290 cm^{-1} decreased in relative intensity.

On the other hand, when TlI plates were used, the surfaces of the plates in contact with the solutions became slightly dark after a prolonged measurement, but no bands due to thallos nitrate¹⁵ were observed.

These results are shown in Figs. 1 and 2, and Tables 1 and 2.

TABLE I

INFRARED FREQUENCIES OF $(\text{CH}_3)_3\text{Sb}(\text{OCOR})_2$ AND $(\text{CH}_3)_3\text{SbBr}_2$ (in cm^{-1})

| $(\text{CH}_3)_3\text{SbBr}_2^a$ | $R = \text{H}$ | | Assignment |
|----------------------------------|--------------------|-----------------------|--------------------------------|
| | Solid ^a | Solution ^b | |
| 3008 vw | 3245 vw | 3289 vw | CH ₂ deg. str. |
| 2915 vw | 3012 w | 3021 vw | |
| | 2933 w | 2941 vw | CH ₂ sym. str. |
| | 2865 w | 2857 m | C-H str. |
| | 2849 w | | |
| | 2841 w | 2703 vw | |
| 1772 vw | | | |
| 1723 vw | | | |
| | 1647 s | 1653 s | C=O str. |
| | 1634 s | | |
| 1400 w | 1408 w | 1404 vw | CH ₃ deg. def. |
| | 1377 m | 1362 m | C-H bend. |
| | 1306 (sh.) w | | |
| | 1250 s | 1233 s | C-O str. |
| | 1231 s | | |
| 1209 vw | | 1221 m | CH ₃ sym. def. |
| 872 s | 875 s | 862 s | CH ₃ rock. |
| | 856 s | | |
| | 840 (sh.) | | |
| | 762 s | 767 s | COO def. |
| 569 m | 583 m | 581 m | SbC ₃ deg. str. |
| | 535 vw | | SbC ₃ sym. str. (?) |

^a Mulls in nujol or hexachlorobutadiene. ^b CCl₄ or CHBr₃ solution.

RESULTS AND DISCUSSION

In the spectrum of trimethylantimony diformate taken in nujol mulls, strong absorption bands are found at 1647, 1634, 1250 and 1231 cm^{-1} . In the spectra of solutions these bands appear at 1653 and 1233 cm^{-1} . These bands are assigned to the

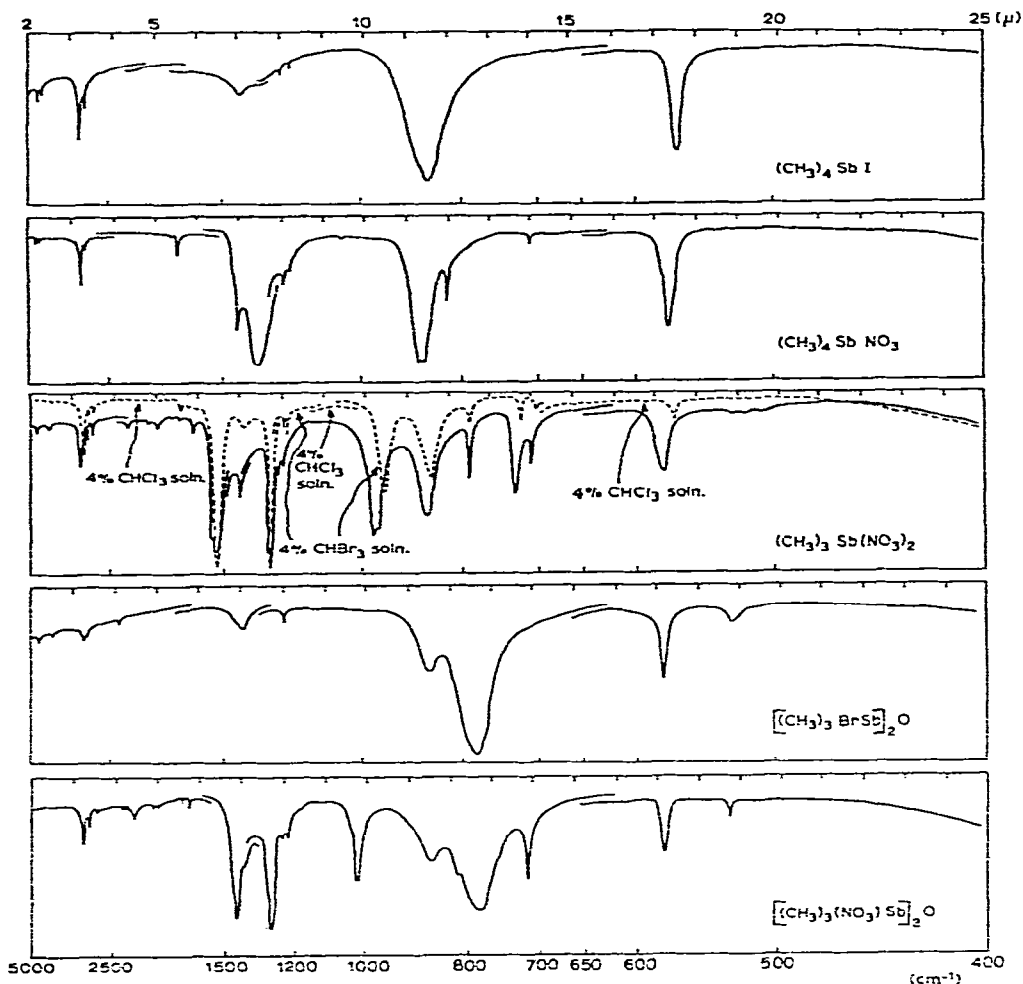


Fig. 2. IR spectra of methylantimony halides and nitrates — mulls in nujol or HCB; ···· solution in CHCl_3 or CHBr_3 .

stretching vibrations of a carboxyl group having a reduced symmetry similar to that of organic esters. The stretching frequencies associated with the $-\text{COO}-$ group of the other carboxylates studied are shown in Table 3.

Data from the spectra obtained in the solid state show that the absorption bands are split, possibly due to crystal lattice effects. The corresponding bands in the spectra of the liquid films and of the solutions occur at essentially the same frequencies as are observed in the solid state spectra. Thus it can be assumed that the configuration of the carboxyl group is the same in the solid and liquid states and in solution.

The band assigned to the $\text{C}=\text{O}$ stretching vibration occurs at a lower frequency and that assigned to the $\text{C}-\text{O}$ stretching vibration occurs at a higher frequency than the frequencies of the corresponding modes in organic esters. This can be ascribed to the increased polarity of the $\text{Sb}-\text{O}$ bond in antimony compounds compared to the $\text{C}-\text{O}$ bond in organic esters. The facts that the dicarboxylates are soluble in organic

TABLE 2
INFRARED FREQUENCIES OF METHYLANTIMONY HALIDES AND NITRATES (in cm⁻¹)

| $(CH_3)_4SbI^a$ | $(CH_3)_4SbNO_3^a$ | $(CH_3)_3Sb(NO_3)_2$ | | $[(CH_3)_3Sb(NO_3)]_2O^b$ | $[(CH_3)_3Sb(NO_3)]_2O^b$ | Assignment |
|-----------------|--------------------|----------------------|------------------------|---------------------------|---------------------------|-------------------------------|
| | | Solids ^a | Solutions ^b | | | |
| 3003 W | 3007 W | 3040 W | 3030 W | 3021 VW | 2994 VW | CH ₃ deg. str. |
| 2915 VW | 2915 VW | 2940 VW | 2947 VW | 2933 VW | 2941 VW | CH ₃ sym. str. |
| | | 2797 VW | 2817 VW | 2740 VW | | |
| | | | | 2499 VW | | |
| | | | | 2033 VW | | |
| | | | | 2000 VW | | |
| 1779 VW | 1795 VW | 1933 VW | | 1862 VW | | |
| 1739 VW | 1748 VW | 1812 VW | | 1724 VW | | |
| | | 1761 VW | 1773 VW | | | |
| | | 1672 VW | | | | |
| | | 1545 (sh.) S } | 1536 S } | 1450 S } | | NO ₂ antisym. str. |
| | | 1527 S } | 1493 W } | 1404 (sh.) W } | 1399 W | CH ₃ deg. def. |
| 1404 W | 1425 M | 1404 W | | | | NO ₂ deg. str. |
| | 1339 S | | | | | NO ₂ sym. str. |
| | | 1490 S } | 1282 S } | 1290 S } | | |
| | | 1274 S } | | | | |
| 1242 VW | 1221 VW | 1242 W | 1244 W | 1236 W | | CH ₃ sym. def. |
| 1212 VW | 1209 VW | 1229 W | 1230 W | 1224 W | 1224 W | NO ₂ sym. str. (?) |
| | 1043 VWV | | | | | N-O str. |
| | | 968 S } | 954 M } | 1018 M } | | |
| | | 959 S } | | | | CH ₃ rock. |
| 867 S | 875 S } | 864 S } | 861 M } | 862 M } | 858 M | NO ₂ def. |
| | 864 S } | | | | | NO ₂ def. |
| | 826 W | | | | | Sb-O-Sb antisym. str. |
| | | 793 W | 794 W | 808 M | 786 S | NO ₂ def. |
| | | 729 M | 725 W | 787 S | | NO ₂ def. |
| | | 707 W | 702 VW | 716 M | | NO ₂ def. |
| 570 M | 706 VW | | | | | SbC ₃ deg. str. |
| | 574 M | 580 M | 573 W | 580 M | 570 M | SbC ₃ sym. str. |
| | | 529 VW } | | 532 W } | 528 W } | |
| | | 521 VW } | | | | (?) |
| | | 508 VW } | | | | |

^a Mulls in nujol or hexachlorobutadiene. ^b CHCl₃ or CCl₄ solution.

TABLE 3

STRETCHING FREQUENCIES OF $-\text{COO}-$ GROUP IN $(\text{CH}_3)_3\text{Sb}(\text{OCOR})_2$ (in cm^{-1})

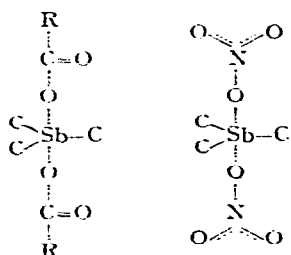
| $R = \text{CH}_3$ | | $R = \text{C}_2\text{H}_5$ | $R = \text{C}_3\text{H}_7$ | $R = \text{C}_6\text{H}_5$ | Assignment | | |
|--------------------|-----------------------|----------------------------|----------------------------|----------------------------|------------|--------|----------|
| Solid ^a | Solution ^b | liquid film | liquid film | solid ^a | | | |
| 1637 s | 1650 s | 1647 s | 1658 s | 1642 s | C=O str. | | |
| 1600 (sh.) s | | | 1653 s | 1631 s | | | |
| 1287 s | | | 1286 s | 1231 s | 1220 s | 1323 s | C-O str. |
| 1274 (sh.) s | | | | | 1299 s | | |

^a Mulls in nujel or hexachlorobutadiene. ^b CCl_4 or CHBr_3 solution.

solvents and that some of them are distillable, suggest that the carboxyl groups are bound to the trimethylantimony group in a manner that is similar to organic esters.

The spectrum of trimethylantimony diformate in solution also suggests that the C_3Sb group is a trigonal plane with the antimony situated at the center. Only one strong band at 581 cm^{-1} was observed in the KBr region. This is due to the C_3Sb degenerate stretching vibration. A planar configuration would have only one infrared active Sb-C stretching mode. Cryoscopic molecular weight determination of trimethylantimony diformate and diacetate in benzene shows that these carboxylates are monomers. This fact also supports the conclusion that in both the solid and solution states $(\text{CH}_3)_3\text{Sb}(\text{OCOR})_2$ has a trigonal bipyramidal configuration, similar to $\text{R}_3\text{SbX}_2^{1,2}$, as shown in Fig. 3.

From Fig. 2 and Table 2, it is clear that, except for three additional bands at 1339 (s), 826 (w) and 706 (vw) cm^{-1} , the spectra of tetramethylstibonium nitrate are quite similar to those of tetramethylstibonium iodide. The latter compound is reported to have an ionic structure, $(\text{CH}_3)_4\text{Sb}^+\text{I}^-$, where the $(\text{CH}_3)_4\text{Sb}^+$ group has T_d symmetry¹⁶. Therefore, these three additional bands are satisfactorily assigned to a nitrate ion having D_{3h} symmetry. In the case of trimethylantimony dinitrate, six bands associated with the NO_3 group are obtained in the NaCl region as shown in Fig. 2. Obviously these six absorption bands are not associated with the nitrate ion having D_{3h} symmetry, but correspond to those of NO_3 group having C_{2v} or lower symmetry. In this compound the antisymmetric stretching frequencies of the NO_2 group are somewhat lower and the symmetric modes are somewhat higher than those of the nitric ester, $\text{CH}_3\text{ONO}_2^{17}$. However, these trends may be explained by considering the polarity of the Sb-O bond as previously discussed. Thus trimethylantimony dinitrate has a trigonal bipyramidal configuration analogous to the structures of the dicarboxylates as is shown in Fig. 3. The double charged ionic structure, $(\text{CH}_3)_3\text{Sb}^{2+}$, proposed

(a) $\text{Me}_3\text{Sb}(\text{OCOR})_2$ (b) $\text{Me}_3\text{Sb}(\text{NO}_3)_2$ Fig. 3. Structures of $(\text{CH}_3)_3\text{Sb}(\text{OCOR})_2$ and $(\text{CH}_3)_3\text{Sb}(\text{NO}_3)_2$.

by Long *et al.*⁵ is based on spectra obtained in KBr disks. Since trimethylantimony dinitrate readily reacts with KBr to form nitrate ion, the basis for this conclusion is apparent. In solution and as nujol mulls, however, the spectra reveals that the nitrate group has C_{2v} symmetry.

Oxybis(trimethylantimony) dinitrate has also been shown to contain a nitrate group with C_{2v} or lower symmetry. Thus in Fig. 2, and Table 2 five bands ascribable to a NO_3 group are readily apparent. A sixth band occurring around 750 cm^{-1} is probably masked by the strong Sb–O–Sb antisymmetric stretching mode. However, in this compound, the antisymmetric stretching frequencies of the NO_2 group are somewhat lower than those of trimethylantimony dinitrate. This suggests that the Sb–O bonds in this compound are intermediate in character between covalent and ionic bonds. Comparison with the spectrum of oxybis(trimethylantimony) dibromide reveals no important differences between the two compounds other than that due to the nitrate group. This further supports the conclusion that the bonding in this compound is of intermediate polarity.

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SUMMARY

Some trimethyl-substituted antimony(V) compounds containing Sb–O bonds such as trimethylantimony dicarboxylates, dinitrate or oxybis(trimethylantimony) dinitrate, were prepared. From the infrared spectroscopic investigation, both in the solid and in solution, and cryoscopic molecular weight determinations in benzene, the following results were obtained. (1) $(CH_3)_3SbX_2$ (where X is OCOR or NO_3) has a trigonal bipyramidal configuration with the C_3Sb group in the same plane and X at the apices. (2) The Sb–O bond in $(CH_3)_3SbX_2$ (where X is OCOR or NO_3) is covalent in nature while the Sb–O bond in oxybis(trimethylantimony) dinitrate is intermediate in character between covalent and ionic bonds.

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