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Synthesis and Characterization of Some New Organo Antimony Xanthates

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Triphenyl stibine dibromide was allowed to react with potassium alkyl or aryl xanthates, which yielded organo antimony xanthates of general formulae $Ph_3Sb(S_2COR)_2$, (where R=methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl and benzoyl), which were characterized through elemental analysis, molecular weight, conductance, T.G.A. and IR spectral data. Infrared spectral data clearly indicates that the xanthate ligand is bonded to organo antimony moiety through the sulphur and not through oxygen molecule.

INTRODUCTION

There has been a considerable interest in the chemistry of metal xanthates and related compounds, because of their analytical and industrial importance.[1] They have considerable commercial value and are used as corrosion inhibitors antifugal agents[2] and stabilizers of poly vinyl chloride.[3] There are a few reviews on metal xanthates.[4-8] Gottardi reported the crystal structure of antimony(III) ethyl xanthate.[9] Khwaja and Cardwell[10] reported the preparation, mass spectral measurement and mechanism for the thermal decomposition of $Sb(S_2COR)_3$, where R=Me, Et, i-Pr, Bu, $PhCH_2$ and cyclohexyl. Winter[11] reported the ir, uv spectra and conductance of ethyl antimony(III) xanthate. In this communication some organo antimony xanthates of the general formula $Ph_3Sb(S_2COR)_2$, where R=Me, Et, Pr, i-Pr, Bu, i-Bu, Am and Bz were prepared and characterized through various physico-chemical techniques.

EXPERIMENTAL

Triphenyl stibine dibromide was prepared from triphenyl stibine according to following equation:

$$(C_6H_5)_3Sb + Br_2 \rightarrow (C_6H_5)_3\ SbBr_2$$

Thus in a typical experiment 7.06 g triphenyl stibine was dissolved in 50 ml petroleum ether (60–80°C). To this was added dropwise bromine solution in petroleum ether (60–80°C) in slight excess (3.3 g) with constant stirring. The stirring was continued for another 30 minutes. The precipitated triphenyl stibine-dibromide was filtered and washed with pet.

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ether (40–60°C) and dried in vacuum. It was recrystallized from benzene, m.pt. 213°C (Lit. value 214–215°C).

The potassium salts of alkyl or aryl xanthates were prepared by refluxing4.2 g KOH pellets and 12.0 g (15.2 ml) absolute ethanol in a 50 ml round bottom flask for about an hour. It was cooled and the mother liquor was separated by decantation. Now 5.7 g (4.5 ml) CS_2 was added to decanted mother liquor slowly with constant stirring and cooled in ice. The solid mass thus obtained was filtered through a sintered glass funnel at pump and washed with several 2.5 ml portions of diethylether. It was dried in a vacuum desiccator over silica gel. Yield=7.4 g, m.pt. 205–208°C. All the physical measurement and estimation of antimony was done as described earlier[12].

Organo antimony xanthates were prepared by the interaction of potassium alkyl or aryl xanthates with triphenyl stibine dibromide in suitable solvents according to the following equation

$$2KEtOCS_2 + (C_6H_5)_3\,SbBr_2 \rightarrow 2KBr + (C_6H_5)_3\,Sb(EtOCS_2)_2$$

The precipitated potassium bromide was filtered off and the organo antimony xanthates were crystallized from the filtrate.

Thus, in a typical experiment 2.56 g (5 m moles) triphenyl stibine dibromide and 1.6 g (10 m moles) potassium ethyl xanthate were stirred for about 2 hrs. in acetone (50 ml). Precipitated potassium bromide was filtered off and from the filtrate excess of solvent was distilled off. 10 ml. diethyl ether was added to the residual solution kept overnight in deep freeze. The colourless crystals of triphenyl stibine bis ethyl xanthate were separated. It was recrystallised from acetone. The crystallised solid was dried in vacuo over anhydrous calcium chloride, m.pt. 195°C, Yield 1.2 g (40%).

RESULTS AND DISCUSSION

All the newly synthesised organo antimony xanthates are sharp melting; white deliquescent solids. They are insoluble in common organic solvents such as methanol, ethanol, diethyl ether and benzene, but are soluble in acetone and nitrobenzene They are stable at room temp. and can be preserved for months without decomposition over anhydrous calcium chloride or silica gel in a vacuum desiccator.

The molecular weights of typical compounds were determined cryoscopically in nitrobenzene. The elemental data are indicate that all the compounds are monomeric and have the general composition $Ph_3Sb(ROCS_2)_2$ (R=Me, Et, Pr, i-Pr, n-Bu, i-Bu, Am or Bz). The molar conductance values of 10^{-3} M solutions of the newly synthesised compounds in nitrobenzene solution clearly indicate that they are nonelectrolytes. These results are in agreement with previous report[12].

TABLE 1

CHARACTERISTIC INFRARED ABSORPTIONS (cm^{-1}) FOR SOME ORGANO ANTIMONY XANTHATES $Ph_3Sb(ROCS_2)_2$

R	C—H deformation modes	C—H in plane deformation	νC—O—S	νC=S	νC—S	νSb—S
Me	1775 s, 1480 vs, 1435 vs	1360 m, 1330 m	1260 s	1000 vs 1015 vs	860 m	—
Et	1575 m, 1480 s, 1438 s	1380 s, 1320 vs	1265 m	1002 vs 1028 s	855 m	—
Pr	1560 m, 1485 s, 1440 vs	1380 w, 1320 m	1270 vs	1000 vs 1022 vs	875 m	345 vs
i—Pr	1580 m, 1485 s, 1440 vs	1380 m, 1335 m	1270 vs	1000 vs 1025 s	858 m	345 vs
Bu	1570 s, 1480 vs, 1430 vs	1380 m, 1322 m	1260 vs	1000 vs 1020 vs	858 s	345 vs
i—Bu	1560 m, 1475 s, 1425 s	1360 m, 1320 m	1260 s	1000 vs 1020 vs	857 m	345 vs
Am	1580 w, 1480 s, 1440 vs	1380 m, 1330 m	1270 s	1000 vs 1020 vs	850 m	348 vs
Bz	1570 m, 1475 s, 1432 vs	1380 w, 1330 s	1270 w	998 vs 1020 vs	850 m	342 vs

TGA of two representative compounds namely triphenyl stibine bis isopropyl xanthate and triphenyl stibine bis benzyoyl xanthate were carried out at a heating rate of 5°/minute. Triphenyl stible bis isopropyl xanthate starts decomposing at 160°C and the decomposition is completed at 260°C leaving behind a non-volatile residue as antimony (III) oxide (theo. 23.37% obs. 23.68%). Triphenyl stibine bis benzoyl xanthate starts decomposing at 240°C and the decomposition is complete at 380°C. The residue after decomposition corresponds to antimony trioxide (Theo. 20.25% obs. 20.33%). These results are in good agreement with previous report on antimony (III) and —(V) halide complexes with schiff bases[13].

The possible assignments for fundamental modes of vibration have been made by a critical comparison of the spectra of newly synthesised compounds with related published work on xanthates. The absorption of diagnostic values are listed in Table 1. The ir bands of particular interest are C—O—C, C=S, C—S and Sb—S stretching frequencies, which have been used to obtain information on the manner in which the xanthate group binds to the antimony metal ion. In the present investigation the absorption in the region 1260–1270 cm^{-1} is assigned to C—O—C clearly indicates that C—O does not take part in coordination to the antimony metal atom 14–19. In the dithiocarbamates a band at *ca* 1000 cm^{-1} has been assigned to the asymmetric CSS stretching mode. The splitting of this band indicates unidentate sulphur coordination, while in bidentate coordination a single intense band in the same region is usually observed[20–25]. This criterion has found successful application in identifying the nature of sulphur bonding in metal xanthate also. The organo-antimony xanthate under investigation shows doublets in the region 990–1028 cm^{-1} due to νC—S absorption, suggesting the unidentate ligating behaviour of the xanthate moiety. A strong absorption band around 855 ± 5 cm^{-1} is assigned as due to νC—S stretching mode on the basis of existing literature [23,26,27], which do not participate in the coordination. Also a single intense band at 345 $\pm$ 3 cm^{-1} in the present xanthate is assigned to Sb—S stretching mode on the basis of earlier report[28]. Thus, the i.r of new organoantimony xanthates indicate that the compounds bear an ester like structure possessing unidentate xanthate group and penta coordinated antimony atom.

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