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THE NATURE OF THE SOLID REACTION PRODUCT FROM TRI-
(p-TOLYL) AMINE AND ANTIMONY PENTACHLORIDE

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ABSTRACT

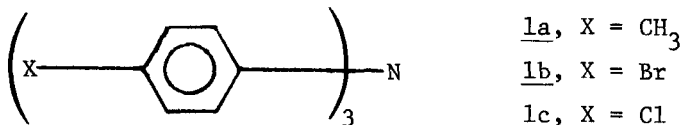
X-ray powder diffraction studies of the solid isolated from interaction of tri-(p-tolyl) amine (TTA) and SbCl_5 establish that this material consists of more than one crystalline phase, a consequence of the reactivity of SbCl_6^- toward TTA.

INTRODUCTION

In 1907, Wieland¹ reported that tri-(p-tolyl) amine (TTA, 1a) interacted with antimony pentachloride (SbCl_5) to give a dark blue crystalline solid assigned the composition TTA.SbCl_5 . We have used this ion-radical salt² in our studies of chemical control of conductivity³ and superexchange⁴ in molecularly-doped polymer films. In the course of this work, we have obtained x-ray powder diffraction data which reveal TTA.SbCl_5 in a new perspective, namely a solid with an approximate composition consisting of more than one crystalline phase. This information is of some consequence since TTA.SbCl_5 has been described⁵ as a possible linear chain antiferromagnet and also studied as a potential catalyst for the oxygenation of dienes.⁶

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FIGURE 1



EXPERIMENTAL

General

Melting points are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York. Cyclic voltammetry was performed as previously reported.⁷ The Debye-Scherrer patterns were obtained on a 114.6mm camera using Ni filtered CuK_α radiation. ESR spectra were obtained using a conventional X-band spectrometer fitted with a dual-matched cavity. The usual precautions, concerning overmodulation and saturation effects, were observed. Spin counting techniques, accurate to $\pm 30\%$, were used to deduce the ion concentrations.

Tetraethylammonium Hexachloroantimonate. This salt was prepared as described previously⁸ to give white needles, mp 293-296° (dec), independent of heating rate and unchanged after storage for one year (lit. (9) mp. 276° (dec)).

Anal. Calcd for C₈H₂₀Cl₆NSb: C, 20.68; H, 4.34; Cl, 45.77; N, 3.01. Found: C, 20.63; H, 4.34; Cl, 45.64; N, 3.06.

Interaction of TTA with SbCl₅. Equimolar quantities of TTA⁹ and SbCl₅, both in chloroform solution were mixed

at room temperature. Slow addition of a volume of benzene at least equal to the used volume of chloroform precipitates a dark blue crystalline solid in yields greater than 65%, m.p. 114-115°(dec) (lit. m.p. 116°(dec)¹, 114-115°)⁵. Rapid addition of benzene to the chloroform solution precipitates a solid with the same melting point which is amorphous by X-ray diffraction.

Anal. Calcd for C₂₁H₂₁Cl₅NSb: C, 42.98; H, 3.58; Cl, 30.28; N, 2.39; Sb, 20.78; calcd for C₂₁H₂₁Cl₆NSb: C, 40.56; H, 3.40; Cl, 34.21; N, 2.25; Sb, 19.58. Found: C, 41.64; H, 3.51; Cl, 30.20; N, 2.25.

The observed analysis corresponds to C_{21.6}H_{21.8}Cl_{5.3}N. Our attempts to obtain single crystals suitable for X-ray diffraction study have not been successful to date. Debye-Scherrer patterns of two separate precipitations show reflections with the following d-spacings (uncorrected for absorption) greater than 2.0Å:

Sample 1: 9.7, 8.8, 8.1 (s = strong), 7.6, 6.9(s), 6.3, 5.3, 4.95(s), 4.70, 4.40, 4.05, 3.75, 3.27, 3.02, 2.92, 2.85, 2.66, 2.50, 2.41, 2.34, 2.19.

Sample 2: 9.0, 8.1(s), 7.6, 6.9(s), 6.3, 6.0, 5.6, 5.1(s), 4.95(s), 4.70, 4.40, 4.30, 4.05, 3.75, 3.27, 2.92, 2.66, 2.57, 2.48, 2.41, 2.19.

While the two patterns have many lines in common, each sample exhibits lines not found in the other. This indicates that "TTA.SbCl₅" precipitates involve at least three different crystallographic phases.

RESULTS AND DISCUSSION

Our observation of different Debye-Sherrer patterns for different preparations of the solid from TTA and SbCl_5 requires that this solid consist of more than one crystalline phase. The presence of more than one crystalline phase in a precipitate of two component organic ion-radical salts has been previously discussed.¹⁰ Our analytical data for the solid are consistent with the approximate composition "TTA. SbCl_5 ". This requires further comment since SbCl_5 interacts with tris-(p-bromophenyl)-amine(1b, TBA) to give a hexachloroantimonate¹ and reaction of SbCl_5 with triphenylmethane and tropyliene¹² gives hexachlorantimonates of the relevant carbocations. We have also observed¹³ formation of a hexachloroantimonate with tris-(p-chlorophenyl) amine (TCA, 1c).

The SbCl_6^- ion is a sufficiently strong oxidant that it ionizes ferrocene.⁸ We observed that addition of $(\text{C}_2\text{H}_5)_4\text{N}^+\text{SbCl}_6^-$ to TTA in acetonitrile colored the solution blue and revealed an absorption maximum at 670 nm, characteristic of TTA^+ .¹⁴ The analogous experiment with TCA revealed no visible change. The greater ease of solution oxidation of TTA vs. TCA is quantitatively revealed in cyclic voltammetry. We observe reversible behavior at +0.81 volts for TTA and +1.13 volts for TCA, in agreement with an earlier study.¹⁵ We suggest that the precipitate with the approximate composition "TTA. SbCl_5 " likely contains SbCl_6^- and a reduced species such as SbCl_5^- , although the possible presence of more complex antimony anions^{8,16,17} is not precluded.

Spin counting techniques using 10GH_z esr were carried out on samples of accurately known geometry and consisted of known amounts of TTA.SbCl₅ dissolved into an inert matrix of polycarbonate and draw-bar coated into 20 μm films.

At room temperature, neat TTA.SbCl₅ exhibits a single line esr spectrum with a width of 1 gauss, $g = 2.0029$; this line broadens on dilution with Lexan.^R Our esr studies of these films reveal a good linear relationship between the number of spins in TTA.SbCl₅ deduced by weight, assuming TTA⁺ as the only paramagnetic species, and the number of spins deduced by spin count. We find no indication of the presence of significant concentrations of paramagnetic antimony species, consistent with earlier work.⁵

The spin susceptibility is Curie-like to ca. 10K^0 , where an antiferromagnetic transition seems to occur, in agreement with other work.⁵ These authors find Curie-Weiss behavior in NMR using the paramagnetic shift, and have investigated the transition using low field esr.

In summary, our analytical and X-ray powder diffraction data establish that the solid with the composition TTA.SbCl₅ contains more than one crystallographic phase. Our esr data for this solid are in satisfactory agreement with previous studies and confirm that the antimony counterions have diamagnetic formulae.

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