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Mass spectroscopy of $SbCl_5$-intercalated graphite

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A mass analysis is presented of ions from stage-1 and stage-2 $SbCl_5$-intercalated graphite ionized by electron bombardment at an energy of 70 eV. The results show that $SbCl_3$ is in both compounds and that Sb_2Cl_6, in the form of a $SbCl_3$-$SbCl_3$ dimer, is present in the stage-1 intercalated compound. There is appreciable $SbCl_5$ or $SbCl_6^-$ only in the stage-1 compound. $SbCl_3$ and $SbCl_4$ are present in stage-2 $SbCl_5$ graphite.

INTRODUCTION

The intercalants in graphite after intercalation of $SbCl_5$ are probably not only $SbCl_5$ molecules. Mössbauer experiments show that the ratio $Sb^{5+}:Sb^{3+}$ is 1.9, which means that Sb is in more than one charge state.[1,2] It has been proposed that the intercalant in the graphite consists of $SbCl_6^-$ and $SbCl_3$.[3,4] However, it has been shown recently that a reaction that forms these products cannot be more than 80% complete.[5] The purpose of this work is to determine the intercalants in graphite by means of mass spectroscopy. Both stage-1 and stage-2 $SbCl_5$ graphite intercalation compounds (GIC'S) are investigated.

Mass spectroscopy has been used previously to investigate several other intercalation compounds. Mass spectra of the binary pentafluoride MF_5 compound consist of ions MF_n^+ with $n<5$.[6] Similarly, the mass spectra of the gases evolved from the intercalants XeF_6, XeF_4, and $XeOF_4$ show none of their predecessors' spectra.[7] AsF_n^+, NbF_n^+, and TaF_n^+ ions with $n \leq 4$ from intercalated compounds have also been reported recently.[8]

Both antimony and chlorine have two stable isotopes. The natural abundances of ^{121}Sb and ^{123}Sb are 57.25 and 42.75 wt. %, respectively, and those of ^{35}Cl and ^{37}Cl are 75.4 and 26.6 wt. %, respectively. This results in a characteristic isotopic cluster abundance pattern for each of the ions that are formed. The pattern is used to identify the ions detected by the spectrometer.

EXPERIMENT

A double-focusing mass spectrometer (model VC 707-F) with a resolution, $m/\Delta m$, of 1000 at the McMaster Regional Centre for Mass Spectroscopy was used for the mass analyses. The samples were heated in the source chamber of the spectrometer from 20 to 350 °C. Vapor from the sample was ionized with bombardment by an electron beam with a typical energy of 70 eV. This produced positive ions that were fragments of intercalated molecules. Mass spectra were taken during the heating and were recorded in a computer for future analysis. The spectra were independent of ionization energy between 35 and 70 eV.

The samples were prepared by the reaction of pieces ($3\times3\times0.5$ mm^3) of highly oriented pyrolytic graphite (HOPG) with liquid $SbCl_5$. The stage-1 compounds were formed with the HOPG pieces in $SbCl_5$ at a temperature of 220 °C for 7 d. The stage-2 samples were made by immersing HOPG in $SbCl_5$ at 100 °C for 3–4 d. X-ray ($00l$) diffraction with sharp diffraction peaks showed that each sample was in a single stage.

EXPERIMENTAL RESULTS

The mass spectrum from the stage-1 compound is shown in Fig. 1. The mass number of the most abundant mass in each cluster is indicated. The doublets at mass numbers 70 and 121 belong to Cl_2^+ and Sb^+, respectively. The clusters between mass numbers of 150 and 300 are from $SbCl^+$, $SbCl_2^+$, $SbCl_3^+$, and $SbCl_4^+$. There is no evidence of $SbCl_5^+$ and $SbCl_6^+$ in Fig. 1. The cluster in the region of mass number 420 is identified with $Sb_2Cl_5^+$. $SbCl_2^+$ is the most abundant from all stage-1 samples. The amount of $SbCl_4^+$ that is detected relative to the other ions varies greatly from sample to sample. It is large in Fig. 1, while for some other stage-1 samples it is only several percent of that of $SbCl_2^+$.

The mass region of the stage-1 compound between mass number 300 and 500 is amplified by a factor of 100 in Fig. 2 to show the most abundant isotope of the $Sb_2Cl_5^+$ cluster with a relative intensity of 100. $Sb_2Cl_4^+$, $Sb_2Cl_3^+$, and $Sb_2Cl_2^+$ mass clusters are also evident in Fig. 2.

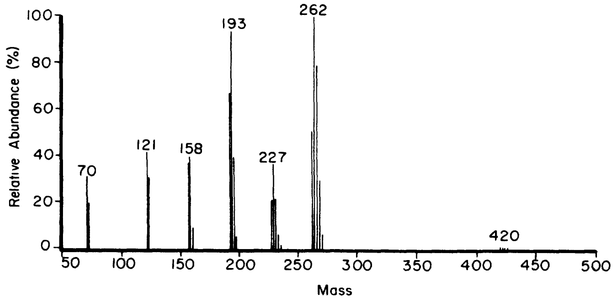

FIG. 1. Mass analysis of stage-1 $SbCl_5$ graphite showing relative abundance vs mass number (M/Z) of ions.

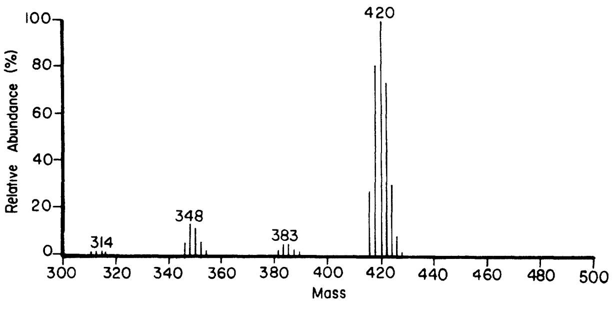

FIG. 2. The mass region $M/Z = 300-500$ of stage-1 $SbCl_5$ graphite.

Figure 3 shows the mass spectrum for a stage-2 compound. The mass clusters starting from the lowest mass are identified with Sb^+, $SbCl^+$, $SbCl_2^+$, $SbCl_3^+$, and $SbCl_4^+$. The detected amount of $SbCl_4^+$ is very small and there is no evidence of $SbCl_5^+$. $Sb_2Cl_5^+$ was not detected in mass scans up to 500.

DISCUSSION

It is assumed that the detected ions are dissociated from molecules arising from the intercalated compound and that a parent of the ions is not formed after release from the graphite. However, a parent from the intercalated sample is not detected because it is not ionized. This is consistent with previous mass-spectroscopy experiments of intercalated compounds. Thus, the heaviest positive ion from $SbCl_5$ is $SbCl_4^+$. This ion is also expected to be the heaviest ion from $SbCl_6^-$ because two Cl^- atoms must be removed to form a positive ion. Thus, the experiment cannot distinguish $SbCl_5$ and $SbCl_6^-$ in graphite.

The possible parents of $SbCl_4^+$ detected in the region of mass 262 are $SbCl_5$ and $SbCl_6^-$. They also result in $SbCl^+$, $SbCl_2^+$, and $SbCl_3^+$. The large amount of $SbCl_4^+$ in Fig. 1 indicates that one or both of $SbCl_5$ and $SbCl_6^-$ are in stage 1. Some could be unreacted $SbCl_5$ because the detected amount of $SbCl_4^+$ is sample dependent. Then, since there is only a small amount of $SbCl_4^+$ in the stage-2 spectra, there is less unreacted $SbCl_5$ in the stage-2 compounds. This is reasonable because the charge transfer is completed in stage-2 compounds with 0.50 units of elementary charge per intercalant molecule.[5] In contrast, the charge transfer in the stage-1 compounds is 0.37 per intercalant molecule and is probably not complete.[9] Ions in the mass spectra could also come from $SbCl_6^-$ in the compounds. However, the concentration of $SbCl_6^-$ cannot be determined because the ions can also come from other molecules.

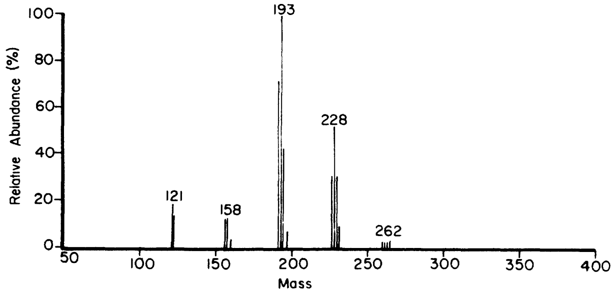

FIG. 3. Mass analysis of stage-2 $SbCl_5$ graphite showing relative abundance vs mass number (M/Z) of ions.

There is a large amount of $SbCl_2^+$ relative to other ions from both stage 1 and stage 2. The probable parent of this excess of ions is $SbCl_3$ in the compounds. Also, the relative abundance of $SbCl_3^+$ ions is much greater than that of $SbCl_4^+$ ions from stage-2 compounds. This could arise from the intercalant $SbCl_4$. Thus, the data are consistent with the view that the intercalant in $SbCl_5$ GIC's result from a disproportionation reaction which forms $SbCl_6^-$ and $SbCl_3$.

The ions $Sb_2Cl_2^+$ to $Sb_2Cl_5^+$ come from Sb_2Cl_6 in the stage-1 GIC. This molecule is expected to be formed by a dipole-dipole pairing mechanism of $SbCl_3$ molecules.[3] The molecular dimer is considered to form the $\sqrt{39}\times\sqrt{39}$ superlattice that is observed at temperatures less than 230 K. At higher temperatures, they are positionally disordered in stage-2 samples with only indications of $\sqrt{39}\times\sqrt{39}$ superlattice ordering up to room temperature. However the $\sqrt{39}\times\sqrt{39}$ ordering is stable up to at least room temperature in stage-1 $SbCl_5$ GIC.[3] Figure 2 taken with a sample temperature of 70 °C shows that the Sb_2Cl_6 dimer is stable above room temperature in the stage-1 GIC and is direct evidence of it.

$SbCl_5$ intercalated graphite is turning out to be a rather complicated compound. Both the 5+ and 3+ states of Sb are detected in Mössbauer experiments.[1,2] Ion and electron microprobes show segregation of the intercalant.[4] Hwang *et al.* then suggest that there are islands of $SbCl_3$ or $SbCl_4^-$ in a background of $SbCl_5$ or $SbCl_6^-$ which are products of unreacted $SbCl_5$ on the surface. X-ray-diffraction measurements[3] are consistent with the presence of two segregated molecular species, $SbCl_3$ and $SbCl_6^-$ and an ordered lattice on $SbCl_3$ dimers. Direct evidence of the molecules that are in the intercalated compound is given by our mass-spectroscopy results. The detected $SbCl_3$ is attributed to the islands observed by ion and electron probes. The unreacted $SbCl_5$ on the surface appears to have different concentrations in stage-1 and stage-2 compounds. It is especially significant that the $SbCl_3$ dimer that has been predicted[3] is observed directly in this experiment.

CONCLUSIONS

The mass spectra of stage-1 and stage-2 $SbCl_5$ GIC ionized by electron bombardment has isotopic clusters of $SbCl_x$ with $x \leq 4$. This gives direct evidence of $SbCl_3$ and $SbCl_5$ or $SbCl_6^-$ in stage-1 $SbCl_5$ graphite. In addition, from the stage-1 compound there are ions $Sb_2Cl_2^+$, $Sb_2Cl_3^+$, $Sb_2Cl_4^+$, and $Sb_2Cl_5^+$. This indicates that there is Sb_2Cl_6 probably in the form of a $SbCl_3$-$SbCl_3$ dimer at temperatures above room temperature in the stage-1 GIC. $SbCl_4$ and $SbCl_3$ are present in stage-2 $SbCl_5^-$ graphite. These results give direct confirmation of the constituents of these rather complicated intercalation compounds.

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