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CHLORINE MONOFLUORIDE ASSISTED INTERCALATION IN GRAPHITE*

STEVEN M. WRIGHT** and ALBERT W. JACHE

Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233, (U.S.A.)

SUMMARY

Phosphorus pentafluoride will form a phosphorus fluoride intercalation compound with graphite in the presence of chlorine fluoride. It will not, under experimental conditions, intercalate when reacted with graphite alone or in the presence of hydrogen fluoride. Apparently, sufficient oxidizing power is needed before intercalation will occur.

INTRODUCTION

Intercalation of certain metal fluorides into graphite has been the subject of many recent studies. While involved in a broader study, we became interested in the intercalation of phosphorus pentafluoride into graphite. An early report of the possible existence of a phosphorus fluoride intercalation compound can be found in the patent literature [1]. It was reported that an intercalation compound was formed by the reaction of graphite with phosphorus pentafluoride in the presence of fluorine. More recently, it was reported that phosphorus pentafluoride would not intercalate when reacted with graphite alone and that it will not interca-

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**Now at University of Wisconsin, Stevens Point.

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late in the presence of HF [2]. During the course of this study, Vogel et al reported that the reaction between $NO_2^+PF_6^-$ and graphite will produce an intercalation compound with the hexafluorophosphate anion as the intercalated specie [3]. We have investigated the possible intercalation of a phosphorus fluoride neat and, in the presence of the chlorine monofluoride, chlorine and hydrogen fluoride. We hoped to find a method by which phosphorus pentafluoride can be intercalated into graphite and to gain some insight into the manner in which it comes about.

EXPERIMENTAL

Reagent grade PCl_5 was used as obtained from the Fischer Scientific Corporation.

We are grateful to Dr. Meshri of Ozark-Mahoning (a division of the Pennwalt Corporation) for the gift of PF_5 which was used as obtained.

High purity Cl_2 was used as obtained from Air Products Corporation.

ClF was prepared in this laboratory by reacting equimolar amounts of Cl_2 and ClF_3 at 200°. The resulting ClF was periodically checked for purity by means of gas chromatography.

Graphite

Two graphite samples were used in this study. Both were obtained from the Asbury Graphite Mills, Incorporated. These samples were characterized by X-ray diffraction and X-ray fluorescence. Both were shown to be of high purity, and highly graphitized. Results obtained with the two samples were essentially the same.

^{19}F nmr spectra were taken on a Joel FX-60-Q spectrophotometer at a frequency of 56.20 MHz. $CFCl_3$ was used as the external reference.

The X-ray diffraction patterns were taken on a North American Phillips Corporation X-ray diffraction unit. Cobalt $K_{\alpha}1$ was the radiation source (1.789A°).

The Graphite PCl_5-ClF System

About 1.0 g of graphite and 2.4 g of PCl_5 were placed in a 0.3 L Monel reaction cylinder. The cylinder was then evacuated and about 18 g of ClF were condensed into the cylinder. The mixture was then heated to 200° for 3 hours.

The Graphite PCl_5-Cl_2 System

About 1.0 g of graphite and 2.4 g of PCl_5 were placed in a 0.3 L Monel reaction cylinder. The cylinder was then evacuated and about 27 g of Cl_2 were added by condensation. The mixture was then heated to 200° for 3 hours.

The Graphite-PF_5-ClF System

About 1.0 g of graphite was placed in a 0.3 L Monel reaction cylinder. The cylinder was then evacuated, and about 2.2 g of PF_5 and 17 g of ClF were condensed into the cylinder. The mixture was then heated to 200° for 3 hours.

The Graphite-PF_5-Cl_2 System

About 1.0 g of graphite was placed in a 0.3 L Monel reaction cylinder. The cylinder was then evacuated, and about 3.2 g of PF_5 and 27 g of Cl_2 were condensed into the cylinder. The mixture was then heated to 200° for 3 hours.

The Graphite-PF_5 System

About 1.0 g of graphite was placed in a 0.3 L Monel reaction cylinder. The cylinder was then evacuated and about 11 g of PF_5 were condensed into the cylinder. The mixture was then heated to 200° for 3 hours.

The Graphite-PF_5-HF System

About 1.0 g of graphite was placed in a 0.3 L Monel reaction cylinder. The cylinder was then evacuated, and about 8.9 g of PF_5 and 1.8 g of HF were condensed into the cylinder. The mixture was then heated to 200° for 3 hours.

RESULTS

Products from the reactions of graphite and PF_5 or PCl_5 in the presence of ClF gave evidence showing the intercalation of a phosphorus fluoride. This evidence was in the form of ^{19}F nmr spectra and X-ray diffraction patterns. The ^{19}F nmr gave a consistent peak about -72 ppm from $CFCl_3$. The X-ray powder diffraction patterns of these products showed an increase in the layer spacing of graphite, from a distance of 3.35A° to a spacing of 6.5 - 6.6A° [3].

The product of the reaction of graphite and PF_5 in the presence of Cl_2 showed some evidence of fluoride uptake. This evidence was in the form of ^{19}F nmr data. However, there were at least 10 times as many pulse repetitions required to obtain an observable peak for these reaction products as for those in which there was other substituted evidence of intercalation. All the lines observed in the X-ray powder diffraction pattern could be attributed to graphite.

All the lines in the X-ray powder diffraction pattern of the products from the reaction of graphite PCl_5 and Cl_2 could be attributed to graphite and PCl_5.

There was no observable peak obtained in the ^{19}F nmr spectrum of the product of the reaction of graphite and PF_5. All the lines observed in the X-ray powder diffraction pattern of the product of the graphite-PF_5-HF system could be attributed to graphite.

DISCUSSION

The following conclusions can be drawn from these results:

As reported earlier [4], PCl_5 will not intercalate, even in the presence of Cl_2 gas.

Consistent with earlier reports [2], when PF_5 is reacted alone or in the presence of HF, there is no indication of intercalation.

When PF_5 reacts with graphite in the presence of Cl_2, there is some evidence that a phosphorus fluoride is taken up by the graphite. Results from this experiment are inconclusive. We are unable to conclude that intercalation does occur, or that it does not.

Intercalation of a phosphorus fluoride is achieved by reacting PF_5 or PCl_5 with graphite in the presence of ClF. It seems obvious that PCl_5 is converted to PF_5 in the ClF. At this point, it is difficult to tell whether the intercalated specie is PF_5 or PF_6^-.* Therefore, no definite conclusion can be made concerning the nature of the phosphorus fluoride intercalated.

However, we do know that a phosphorus fluoride is intercalated only in the presence of a reasonably strong oxidizer (F_2, ClF, NO_2^+ and perhaps Cl_2). In the absence of an oxidizer, it appears that intercalation does not occur (PF_5 alone or with HF). Note also, that for those systems where a phosphorus fluoride intercalation compound is definitely formed, the hexafluorophosphate is present ($NO_2^+PF_6^-$) or can be formed _in situ_ (F_2, ClF). These results would indicate that the oxidation of graphite and the formation of the hexafluorophosphate anion are important steps in the reaction pathway.

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*These products give ^{19}F nmr resonances about -72 ppm from $CFCl_3$. The resonance for $K^+PF_6^-$ is at -69.84 ppm. For PF_5, the fluorine resonance is at -75.84 ppm.

This is consistent with other observations which indicate that a fluoride will intercalate only if it has a relatively high oxidizing power [5]. When there is not sufficient oxidizing capabilities, an additional oxidizer must be added; as in the case of PF_5.

This study has developed another method for intercalating a phosphorus fluoride. Although the exact nature of the fluoride and the mechanism by which it is intercalated are speculative, the results seem to lend support to the idea that the graphite is oxidized during the reaction. Although oxidation is indicated during the mechanism, our results do not prove which phosphorus fluoride is actually intercalated.

Since this work was initially reported, Ebert *et al* [6] have reported on a magnetic resonance study of intercalates of this type and have given further insight into the nature of the compounds.

Preliminary experiments reacting graphite and ClF together with a third reactant were carried out with Mo, W, or Sb as the third reactant. Results from the preliminary experiments indicate that when one of these metals is reacted with graphite and ClF, a metal fluoride intercalation compound is formed. These observations are consistent with other reports [5].

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