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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Synthesis and properties of graphite intercalation compounds with HNO_3, SbF_5 and $FeCl_3$ have been studied with an eye toward insertion mechanism and novel highly conducting compounds. Virtually all "acceptor" type compounds are formed by oxidation reactions initiated at the basal planes. Adducts of $NOCl$-$FeCl_3$ have been shown to be new oxidative intercalants. Electrical properties of graphite nitrate are relatively insensitive to the neutral HNO_3 content.

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BRIEF OUTLINE OF RESEARCH FINDINGS

RESEARCH GOALS

The research was initiated with a three-fold purpose: (1) determine the mechanism of preparation of graphite intercalation (in particular the so-called acceptor compounds); (2) to relate structure and properties of these compounds; and (3) to prepare new intercalation compounds of high electrical conductivity. The proposal indicated that the focus of the research could be on intercalation by HNO_3, SbF_5 and $FeCl_3$.

SUMMARY OF RESULTS

Research supported by this grant was instrumental in leading to the conclusion that virtually all graphite intercalation reactions that give acceptor compounds are oxidation reactions. In the case of HNO_3 intercalation, graphite is oxidized by NO_2^+ ions with formation of free NO_2 and insertion of HNO_3 and NO_3^-. In the case of intercalation by antimony pentafluoride, the SbF_5 oxidizes the lattice and is reduced to SbF_3 (which is excluded from the lattice); SbF_6^- ions and SbF_5 molecules are inserted during the process.

In the case of the nitric acid intercalation compound, it was established that the neutral HNO_3 molecules are labile and can be moved in and out of the lattice by varying the partial pressure of HNO_3 in equilibrium with the intercalation compound. An extraordinarily important observation was that, to a first approximation, the electrical conductivity of the intercalation compound is independent of neutral molecule content.

Work on the mechanism of intercalation by $FeCl_3$ was, on the one hand frustrating and inconclusive, but on the other hand led to a significant discovery. One can postulate that $FeCl_3$ could oxidize graphite, be reduced to $FeCl_2$ and insert $FeCl_4^-$ along with $FeCl_3$ neutral molecules. Also, $FeCl_3$ gives $FeCl_2$ and Cl_2 upon heating. The $FeCl_3$ and Cl_2 could form a complex $FeCl_4^-$ ... Cl^+ which could oxidize the graphite lattice through the chlorine cation - against inserting $FeCl_4^-$ ions. Finally, $FeCl_2$ solid and $FeCl_3$ vapor are in equilibrium with Fe_2Cl_8 gas, which, if it were inserted, would effectively intercalate $FeCl_2$. Much effort in developing analytical techniques for establishing the stoichiometry failed to pin down this mechanism. Our best interpretation of the data is that both mechanisms are operative, leading to confusing results.

To cast more light on the nature of $FeCl_3$ intercalation compounds, we invented a new method of inserting $FeCl_4^-$ ions. Adducts can be prepared from $FeCl_3$ and NOCl. They are low melting partially covalent salts with a formula $NOFeCl_4$. They react with graphite giving highly conductive compounds. In this case, $FeCl_4^-$ is the only plausable ion that could have been inserted.

Finally, we conclude from many of our experiments that attack of the oxidizing agent is on the pi election system in the basal planes.

PUBLICATIONS

1. "Conditions for Intercalation of Graphite with Pure Nitric Acid", W.C. Forsman, J. Hoffman and F.L. Vogel, paper presented at annual meeting of American Chemical Society, New Orleans, March 27-30,1977.

2. "Electrical Resistivity of Graphite Nitrates", F.L. Vogel, C. Zeller and W.C. Forsman, Ext. Abs. Prog., 13th Bienn, Conf. Carbon, 151 (1977).

3. "Chemistry of Graphite Intercalation by Nitric Acid", W.C. Forsman, F.L. Vogel, D.E. Carl and J. Hoffman, Carbon 16, 269 (1978).

4. "Electrical Resistivity of Graphite Intercalated with Ferric Chloride", (abstract), J.B. Perrachon, C. Zeller and F.L. Vogel, Bull. A.P.S. 23, 219

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8. "Vapor Phase Intercalation by $AlCl_3$-HCl Mixtures", K. Leong and W.C. Forsman, Ext. Abs. Prog., 15th Bienn. Conf. Carbon, 356 (1981).

9. "Intercalation of Graphite with the Adducts of Nitronyl Chloride and Metal Chlorides", K. Leong, W.C. Forsman and F.L. Vogel, Ext. Abs. Prog., 15th Bienn. Conf. Carbon, 398 (1981).

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LIST OF DEGREES AWARDED

Master of Science of Engineering (M.S.E.) Degree in Chemical Engineering awarded to Jeffery Hoffman, 1976.

M.S.E. in Chemical Engineering awarded to Theodore Dziemianowicz, August, 1980.