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ADMECHANISM OF INSERTION IN HIGHLY CONDUCTING GRAPHITE INTERCALAT--ETC(U:
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### Key Words
- Intercalation compounds
- Electrical conductivity
- Intercalation mechanism
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 HNO₃, SbF₅ and FeCl₃.

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 HNO₃ intercalation, graphite is oxidized by NO₂⁺ ions with formation of free NO₂ and insertion of HNO₃ and NO₃⁻. In the case of intercalation by antimony pentafluoride, the SbF₅ oxidizes the lattice and is reduced to SbF₃ (which is excluded from the lattice); SbF₆⁻ ions and SbF₅ molecules are inserted during the process.

In the case of the nitric acid intercalation compound, it was established that the neutral HNO₃ molecules are labile and can be moved in and out of the lattice by varying the partial pressure of HNO₃ 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 FeCl₃ was, on the one hand frustrating and inconclusive, but on the other hand led to a significant discovery. One can postulate that FeCl₃ could oxidize graphite, be reduced to FeCl₂ and insert FeCl₄⁻ along with FeCl₃ neutral molecules. Also, FeCl₃ gives FeCl₂ and Cl₂ upon heating. The FeCl₃ and Cl₂ could form a complex FeCl₄⁻ ... Cl⁺ which could oxidize the graphite lattice through the chlorine cation - against inserting FeCl₄⁻ ions. Finally, FeCl₂ solid and FeCl₃ vapor are in equilibrium with Fe₂Cl₃ gas, which, if it were inserted, would effectively intercalate FeCl₂. 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 FeCl₃ intercalation compounds, we invented a new method of inserting FeCl₄⁻ ions. Adducts can be prepared from FeCl₃ and NOCl. They are low melting partially covalent salts with a formula NOFeCl₄. They react with graphite giving highly conductive compounds. In this case, FeCl₄⁻ is the only plausible ion that could have been inserted.

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


LIST OF PERSONNEL SUPPORTED

Dr. F.L. Vogel, Research Professor of Electrical Engineering and Science
Dr. W.C. Forsman, Professor of Chemical Engineering
Jeffery Hoffman, Graduate Student in Chemical Engineering
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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.