

MECHANISM FOR FORMATION OF GRAPHITE "ACCEPTOR COMPOUNDS"

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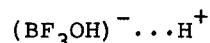
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A review of the intercalation literature suggests that a single mechanism accounts for most known reactions that lead to so-called acceptor compounds. In many of the well documented cases, it is clear that before intercalation can take place, the graphite lattice must first be attacked by an electrophilic reagent. As the reagent removes electrons from the graphite, negative ions, accompanied by neutral molecules, diffuse into the lattice. This is undoubtedly the case in the formation of the aluminum chloride intercalation compound.

It has been established that, when acting separately, neither chlorine gas nor the vapor of AlCl_3 will intercalate the graphite lattice (1). A mixture of the two will, however, cause rapid intercalation (1). This is clearly an example of a Friedel-Crafts type process (2). Most probably, the complex $\text{AlCl}_4 \cdots \text{Cl}^+$ is formed at the graphite-vapor interface by adsorbed AlCl_3 and Cl_2 . It extracts electrons from the lattice and releases chlorine atoms, which couple to regenerate chlorine gas. The AlCl_4 then diffuses into the lattice along with neutral AlCl_3 molecules.

Although it has been reported that the Friedel-Crafts catalyst FeCl_3 can be intercalated without the addition of Cl_2 gas (3,4), Rüdorff, et al. (5) pointed out that at intercalation temperatures FeCl_3 decomposes to generate enough chlorine to effect intercalation by the mechanism described above. Although there is less detail given in the literature on either reaction conditions or characterization of products (6), the above comments on intercalation by FeCl_3 apply equally well to ZnCl_2 , BeCl_2 , ZrCl_4 , NbCl_5 and TaCl_5 - all known to be Friedel-Crafts catalysts (2).

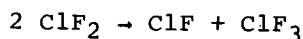
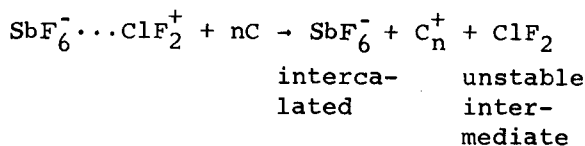
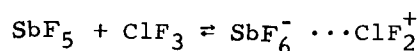
Although pure BF_3 does not intercalate, introducing small amounts of water into the reacting system effects rapid intercalation (7). This is readily explained by attack on the graphite by the highly electrophilic $\cdots \text{H}^+$ of the well known complex (2)



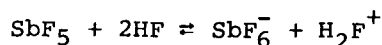
Ubbelohde (8) wrote a balanced reaction for the formation of graphite nitrate that gives NO_2 as a side product. This suggests that intercalation is effected by attack on graphite by nitronium ions, NO_2^+ , which capture electrons and generate NO_2 . In a series of experiments from this laboratory, we recently established that NO_2 is indeed generated during intercalation of highly oriented pyrolytic graphite by the vapor of 100% HNO_3 . There is thus little doubt about the role played by nitronium ions in the formation of graphite nitrate.

It is important to note, however, that after formation of a 2nd stage compound, molecular HNO_3 could be moved in and out of the intercalated lattice by adjusting its partial pressure without concomitant oxidation or reduction of the graphite. Varying the HNO_3 content between apparent 2nd and 4th stages had little effect on electrical conductivity and lattice spacing (9).

Intercalation compounds based on AsF_5 and SbF_5 are of special interest because of conflicting evidence concerning their mechanism of formation. Opalovskii (10) reported that ClF was evolved when graphite was intercalated in a mixture of SbF_5 and ClF_3 , which suggests the mechanism

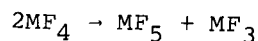
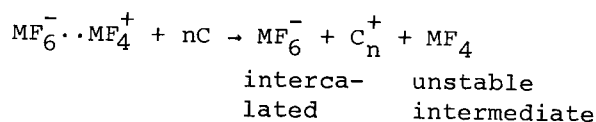
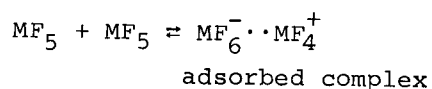


Graphite is also readily intercalated with liquid mixtures of SbF_5 and HF . The well-known electrophilic species in this mixture is H_2F^+ generated by the reaction (11)



If graphite is oxidized by H_2F^+ , however, either H_2 must be liberated or Sb^{V} must be reduced to Sb^{III} . We have established that no H_2 is formed during intercalation; although Sb^{III} was found in the reaction mixture, we have not satisfied ourselves that it could not have been formed by a side reaction. This must be done before its presence represents conclusive evidence for the proposed mechanism.

Both SbF_5 and AsF_5 intercalate graphite without addition of co-reagents, and there is evidence the intercalation involves only diffusion into the graphite lattice followed by electron transfer (12,13). An alternative mechanism involving electrophilic attack would be:



Lin (14) reports that AsF_3 is evolved during intercalation by pure AsF_5 . In addition, we have identified substantial quantities of SbF_3 in the reaction mixture after liquid phase intercalation by SbF_5 , but we have not yet established beyond doubt that it could not have been introduced by a side reaction. Consequently, at this writing it is still not established whether or not intercalation by AsF_5 and SbF_5 is by simple diffusion and electron transfer, or by oxidation of graphite by M^{V} , which is reduced to M^{III} , accompanied by diffusion of MF_6^- and MF_5 (and possibly MF_3) into the lattice.

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