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NEW ASPECTS OF THE INTERCALATION OF GRAPHITE BY FLUORINE AND FLUORIDES

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The intercalation of graphite, by fluorine and by Lewis acid fluorides both in the absence and presence of fluorine, has been studied. A thermodynamic threshold has been established for the oxidative intercalation by hexafluoro-anionic species. When $-\Delta G^\circ_{298}$ for processes such as (a) $3/2MF_5(g) + e^- \rightarrow MF_6^- + \frac{1}{2}MF_3$ or (b) $MF_5(g) + \frac{1}{2}F_2(g) + e^- \rightarrow MF_6^-(g)$, or (c) $MF_6(g) + e^- \rightarrow MF_6^-(g)$ exceed 120 kcal mole^{-1}, spontaneous intercalation of the graphite usually occurs. Thus graphite is not intercalated by PF_5, but is, by a mixture of PF_5 and F_2. The $-\Delta G^\circ_{298}$ for (a) = 86 and for (b) 140 kcal mole^{-1}. PF_3, at ∿ 20°, reduces second and higher stage salts: $2C_x^+PF_6^-(c) + PF_3(g) \rightarrow 2x\ C(c) + 3PF_5(g)$. At ∿ 20°, $AsF_5(g)$, with graphite, in 1:8 molecular stoichiometry, yield ∿ C_8AsF_5, which loses AsF_3 and AsF_5 under vacuum to $C_{22}AsF_6$. The last is a mixture of first and second stage salts, for which the occupied gallery height, I_c, = 7.6 Å. Repeated treatment with AsF_5 yields C_nAsF_6, which approaches a pure first stage of composition $C_{14}AsF_6$, I_c = 7.6 Å. The latter can be made in one step from interaction of graphite with the stronger oxidizers: Solid O_2AsF_6 (no solvent), or $AsF_5(g)$ with F_2. In $C_{14}AsF_6$ X-ray diffraction data have established that the F ligands of the AsF_6^- with threefold F atom sets nestled in contiguous hexagons of the graphite. The O_h symmetry of the AsF_6^- constrains the enclosing carbon-atom layers to be in AB or AC relationship (as in graphite). Addition of AsF_3 or AsF_5 to the I_c = 7.6 phases, increases I_c to ∿ 8Å and the graphite sheets are then eclipsed. This arrangement provides for greater disorder in placement of the guests. Removal of volatiles restores the AB or AC stacking and I_c = 7.6 Å. $C_{14}AsF_6$ is the anticipated limiting composition for a nestled first-stage salt. For kinetic reasons graphite is not intercalated by F_2 alone, but molecules or ions which form readily reversible complexes with F^- (such as HF) bring about spontaneous intercalation of F. In the presence of $HF(\ell)$, graphite intercalates F_2 as hydrofluoride salts to a second stage limit. As intercalation of F_2 proceeds and a first stage product is formed, the fluorine becomes bound to the carbon. The fluorination can be carried out electrochemically and is reversible to a composition approximating $C_{2.5}F$. With F_2 gas as oxidant the limiting composition is close to C_2F. The last is an insulator. At all compositions to C_2F, the carbon-atom sheets remain flat, and the C-C distances close to those in graphite. ^{19}F n.m.r. and ESCA data show the C-F bonds to be semi-ionic and that carbon, not bound to F, to be closely akin to graphite carbon. Bonding models will be discussed.