

Acid Salts of Graphite: Large or Small Fractional Ionization?

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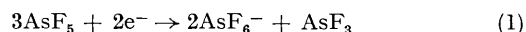
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Summary Evidence for small fractional ionization in C_8AsF_5 and related compounds is summarized; it is argued that the strongly metallic character of these compounds may in fact not be dominated by charge-transfer effects.

THIS communication deals with the similarities and differences among several acid salts of graphite *vis-a-vis* intercalant ionization and electronic properties. They are: C_8AsF_5 (I)¹ which is the 300 K equilibrium stoichiometry for this reactant; $C_{10}AsF_5$ (II)² obtained from (I) by mild pumping; C_8AsF_6 (III)³, obtained by treating graphite with $O_2^+AsF_6^-$; C_8OsF_6 (IV)³; and $C_{12}SO_3F$ (V)³. All five are blue stage 1 compounds. The screened plasma frequencies of (I),⁴ (III),⁵ and (V)⁵ are all *ca.* 1.8 eV and we can assume similar values for (II) and (IV). Thus the density of free carriers contributing to electrical conduction does not vary appreciably. The acid salt model implies a 1:1 correspondence between intercalant ionization and free carriers, so one expects similar fractional ionization for all the species considered here. This model does not apply to some alkali metal compounds in which a fraction of the transferred electron forms a covalent bond with carbon p_z orbitals.⁶

Bartlett *et al.*³ recently presented strong evidence for a high degree of intercalant ionization in (I)—(IV), the most convincing being the large Curie term in the susceptibility of (IV) consistent with $C_8^+OsF_6^-$. X-Ray absorption

spectra of (III) exhibit one line characteristic of As^{5+} which would be consistent with either AsF_6^- or AsF_5 as the intercalant species. Compound (II) shows an additional line which is half as strong attributed to As^{3+} , hence the suggestion that (II) contains AsF_6^- as active species and AsF_3 neutral spacers. However, the n.m.r. spectrum of the same compound⁷ shows only one chemical shift consistent with AsF_5 or AsF_6 but not AsF_3 . Fluorine exchange is probably insufficient to obscure in the n.m.r. spectrum a 1/3 fraction of As^{3+} , which is implied by the X-ray data and by the usual oxidation reaction (1).



Compound (I) has been studied in detail, principally because its stage 2 composition $C_{16}AsF_5$ exhibits conductivity parallel to the layers (σ_a) comparable to that of Ag and Cu at 300 K.⁸ The stoichiometry C_8AsF_5 has been verified many times to $\pm 0.05\%$ by weight uptake. Although the molar ratio C:AsF₅ of 8:1 has not been checked, it is strongly suggested by recent pulsed n.m.r. studies which show that the disorder responsible for motional narrowing of the ¹⁹F resonance is only short range.⁹ Thus on average AsF_5 molecules are likely to be found on every hexagonal site in the 2-dimensional octal structure, as in KC_8 .†

Furthermore, if AsF_5 were oxidized to an appreciable extent, some AsF_3 should appear in the vapour over the compound, especially after pumping with the compound at

† Smaller molecular species would probably be found in the alternative hexal close-packed arrangement analogous to LiC_6 (see ref. 6), *e.g.* C_6HNO_3 .

ambient temperature. In all cases, however, the molecular weight of the gas pumped off corresponds to unreacted or deintercalated AsF_5 .^{1,10}

In the absence of evidence to the contrary, therefore, it may be tentatively concluded that in (I) the intercalated species is AsF_5 and not AsF_6^- . Charge-transfer would lead to AsF_5^- which is paramagnetic. However, the susceptibility is temperature independent, any possible Curie contribution being <0.02 B.M.,⁹ thus the fractional ionization must be quite small. A simple analysis of the screened plasma frequency is consistent with at most 10% ionization.⁴ Given the similarity of metallic reflectance spectra, the same applies to compounds (III) and (V).

Bartlett's note and the results discussed above lead to the curious deduction that there exist graphite salts with either large or small ionization and that their electronic properties are not widely different. In fact, σ_a measurements⁵ on early specimens of (III) and (V) prepared by Bartlett's group gave lower values than (I). If correct, this deduction would invalidate the ionic salt model. Note that σ_a of (IV) has not been measured. This compound presents the best evidence for large ionization,[†] but since it is blue, the screened plasma frequency, and hence carrier density, is no larger than for the others. If σ_a of (IV) turns out to be

unusually large, therefore, it will be due to advantageous carrier scattering properties rather than greater charge transfer. Alternatively, one might argue that the relatively constant layer spacing, *ca.* 8 Å, leads to similar σ_a for all the compounds discussed, in view of the empirical correlation which exists between σ_a and anisotropy.¹¹

In the halogen compounds, both chemical and electronic measurements imply small charge transfer.¹² Salts of protonic acids like H_2SO_4 and HNO_3 are easier to analyse chemically, the former exhibiting two ¹H n.m.r. shifts¹³ and the latter yielding NO_2 gas and water as products according to the reaction: $2\text{HNO}_3 \rightarrow \text{NO}_2^+$ (oxidizes graphite and is liberated) + NO_3^- (intercalates) + H_2O .¹⁴ For HNO_3 one finds 1 ion per 4–5 neutral species. It is clear that elemental analyses are needed to complete the picture for Lewis acid intercalants, particularly the metal:halogen ratio in (I)–(IV). The possibilities remain that the ionic salt picture is incorrect and/or the electronic properties are dominated by structural rather than chemical variables.

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† Note however that whereas local paramagnetism of AsF_5^- could only be attributed to unpaired electrons in valence orbitals, Os halides may have contributions from partially filled *d*-shells independent of the net charge on the molecule. This is in fact suggested by Bartlett's observation of antiferromagnetic coupling in (IV).

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