

## Doping of (CH)<sub>x</sub> Films to the Metallic State with Metal Hexafluorides

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Conductivity measurements have shown that exposure of (CH)<sub>x</sub> film to the vapours of a number of metal hexafluorides causes it to be doped to the metallic regime.

Striking analogies between graphite compounds of the type C<sub>8n</sub>MF<sub>x</sub> and doped polyacetylene compounds such as [CH(MF<sub>x</sub>)<sub>y</sub>]<sub>n</sub>, where the intercalant, *viz.* dopant, can be AsF<sub>5</sub>, SbF<sub>5</sub>, IF<sub>5</sub>, *etc.*, have been demonstrated.<sup>1</sup> Notably, in both cases, the electrical conductivity of the resulting compound is enhanced markedly over that of the untreated material.<sup>2,3</sup> However, significant differences also occur. For example, while iodine and chlorine do not intercalate into graphite, they dope polyacetylene to the metallic state.

The behaviour of hexafluorides towards graphite has recently been investigated.<sup>4</sup> Those with higher electron affinities, such as OsF<sub>6</sub>, IrF<sub>6</sub>, and PtF<sub>6</sub>, intercalate into graphite. The nature of the resulting compounds is not certain, but they have been formulated as salts of the type C<sub>8</sub><sup>+</sup>MF<sub>6</sub><sup>-</sup> (or in the case of PtF<sub>6</sub> as C<sub>12</sub><sup>2+</sup>PtF<sub>6</sub><sup>2-</sup>). Less oxidizing hexafluorides, such as WF<sub>6</sub> and ReF<sub>6</sub>, do not intercalate.<sup>4</sup> Since polyacetylene is more easily oxidized than graphite, a much wider range of

hexafluorides should dope it to the metallic state. The following work shows that this is indeed the case.

The polyacetylene used had a *cis:trans* ratio of approximately 1:1 as determined by i.r. spectroscopy.<sup>5</sup> Samples were mounted in a 4-point jig in an all-Kel-F reactor.<sup>6</sup> Additional samples were kept in close proximity to the electrodes for parallel weight uptake measurements. Comparison of the weight uptake by these pieces with that of the clamped samples showed the same stoichiometry within experimental error. The (CH)<sub>x</sub> was exposed to constant pressures of the hexafluorides by maintaining the latter in a reservoir at a fixed temperature.

Resistances of the (CH)<sub>x</sub> films dropped very rapidly upon first exposure to the vapours. The final conductivity attained was related to the pressure of the hexafluoride except at high pressures when the conductivities often decreased markedly after an initial increase. After doping at a given pressure for

Table 1

| Hexafluoride     | Composition MF <sub>6</sub> : (CH) <sub>x</sub> | Maximum conductivity <sup>a</sup> /<br>Ω <sup>-1</sup> cm <sup>-1</sup> | Colour   |
|------------------|---|---|--|
| SeF <sub>6</sub> | 0.085   | 180   | blue   |
| TeF <sub>6</sub> | 0.081   | 235   | golden-yellow                                  |
| MoF <sub>6</sub> | 0.11  | 70  | golden-yellow<br>(blue at high concentrations) |
| WF <sub>6</sub>  | 0.087   | 350   | golden-yellow                                  |
| UF <sub>6</sub>  | 0.19  | 142   | golden-yellow                                  |
| ReF <sub>6</sub> | 0.21  | 230   | golden-yellow                                  |
| IrF <sub>6</sub> | 0.02  | 50  | black  |

<sup>a</sup> Values may not be optimum since conductivities are highly dependent on experimental parameters such as temperature and pressure.

some time, samples were pumped until constant conductivity was reached, and then weighed in a dry box.

With the exception of  $\text{SF}_6$ , all the hexafluorides in Table 1 doped polyacetylene to the metallic state and their maximum conductivities and corresponding compositions based on weight increase are presented.

The maximum conductivities attained with the 5d transition-metal hexafluorides indicate that they may be correlated with their electron affinities. With stronger oxidizing hexafluorides lower conductivities are attained. This may be due to partial fluorination of the host matrix, a phenomenon which has also been observed with graphite compounds.<sup>1</sup>

Curves of conductivity vs. degree of doping were obtained for  $\text{WF}_6$ ,  $\text{UF}_6$ , and  $\text{MoF}_6$ . Their shape is similar to that obtained with a number of other dopants,<sup>2</sup> the conductivity increasing sharply over several orders of magnitude at low concentrations until a point is reached where additional doping has little further effect. This change in behaviour at critical composition has been attributed to a semi-conductor-to-metal transition<sup>7</sup> and, in the cases of  $\text{MoF}_6$ ,  $\text{WF}_6$ , and  $\text{UF}_6$ , is paralleled by significant changes in their e.s.r. spectra. The change in the nature of the e.s.r. signal in each case is observed at approximately the same dopant:host ratio as in the  $[\text{CH}(\text{AsF}_5)_y]_n$  system<sup>8</sup> and it seems likely, therefore, that the spectra arise from changes in the electronic nature of the host polyacetylene rather than from the dopant. Analysis of the line shape shows that at high doping levels the line shape becomes asymmetric, characteristic of metallic behaviour.<sup>9</sup>

It is reasonable to assume that transition-metal hexafluorides are reduced to stable lower-valent states such as  $\text{MF}_6^-$  or  $\text{MF}_6^{2-}$  (or in the case of  $\text{SeF}_6$  or  $\text{TeF}_6$  to  $\text{MF}_5^-$ ) when incorporated into the host. Mass spectra of  $\text{CH}(\text{WF}_6)_x$  and  $\text{CH}(\text{TeF}_6)_x$  species at ca. 200 °C have shown the presence of released  $\text{WF}_4^+$  and  $\text{TeF}_4^+$  species. The parent ions,  $\text{WF}_5^+$ ,  $\text{TeF}_6^+$ , or higher oxidation-state fluorides were not detected.

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