Doping of $(CH)_x$ Films to the Metallic State with Transition Metal Pentafluorides

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Conductivity measurements have shown that exposure of $(CH)_x$ films to metal pentafluorides causes them to be doped to the metallic state; an inverse correlation exists between maximum conductivity attainable and the fluoride ion affinity of the pentafluoride.

It is now a well established fact that, using chemical or electrochemical doping,[1] the electrical conductivity of polyacetylene, $(CH)_x$, can be increased by many orders of magnitude so that its insulator properties change to those of a metal. The list of dopants is continually increasing and appears to be by no means exhausted. Most attention has focused, however, on acceptor compounds such as AsF_5 or SbF_5 or the halogens, bromine and iodine.

The term 'doping' refers to the redox reaction between the polymer and the 'dopant'. Its nature is not yet completely understood. It is therefore desirable to study families of doped polymers in which the dopants have similar chemical composition, but different electronic configurations, so that the effect the latter may have on the physical properties of the doped polymer can be studied systematically.

Such a family of dopants has recently been reported: namely, the metal hexafluorides.[2] Although the chemical reaction occurring upon doping with hexafluorides has not yet been ascertained, it has been shown that for the 5d hexafluorides, the maximum electrical conductivities attainable vary inversely with their electron affinities.[2,3] This may be due to increased charge localisation leading to lower mobilities of the charge carriers, as has also been suggested for some of the analogous graphite intercalation compounds.[4]

We now report data for a number of metal pentafluorides (MF_5). We note that a total of 24 pentafluorides are known.† Thermochemical data available are sparse, but it appears that correlations similar to those for the hexafluorides exist.

Experimentally, doping with metal pentafluorides is somewhat more difficult, because of their much lower volatilities.[5] Most transition metal pentafluorides have boiling points

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† Those of V, Nb, Ta, Cr, Mo, W, Tc, Re, Ru, Os, Rh, Ir, Pt, Au, Pa, U, Np, P, As, Sb, Bi, Cl, Br, and I.

Table 1

Dopant	$MF_5/(CH)_x$ Molar ratio	Maximum conductivity/ Ω^{-1} cm^{-1}	$-\Delta H^a$/ kcal mol^{-1f}
NbF_5	0.16	229	*ca.* 70[b]
TaF_5	0.18	147	92.6[c]
MoF_5	0.19	28	98.8[d,e]
WF_5	0.04	2.9	117.6[d,e]
RuF_5	0.02	4.8	
BiF_5	0.005	0.2	
BiF_5	0.002	0.006	

[a] Fluoride ion affinity for the reaction $MF_5(c) + F^-(g) \rightarrow MF_6^-(g)$. [b] Best estimate, R. D. Peacock, personal communication. [c] Ref. 8. [d] Ref. 9. [e] Ref. 10. [f] 1 cal = 4.184 J.

above 200 °C, but many decompose with disproportionation at much lower temperatures.[5] Weighed polyacetylene strips with a *cis*: *trans* ratio *ca.* 1 : 1 were mounted in a four-point jig in a Kel-F reactor.[2] The powdered pentafluoride samples were placed at the bottom of the Kel-F tube in close proximity to the mounted $(CH)_x$ film. All manipulations were carried out in an inert atmosphere (N_2) glove box. The nitrogen atmosphere in the reactor slowed diffusion of the pentafluorides to such an extent that no changes of resistance were observed for periods up to 24 h. As the nitrogen was pumped off, the resistances of the films dropped very rapidly indicating that MF_5 vapours were being pumped across them even at the low vapour pressures obtaining at ambient temperature. Although extrapolations over large temperature ranges are uncertain, it is estimated that the MF_5 vapour pressures were of the order of several μmHg. When the rate of change of resistance had slowed considerably, pumping was discontinued and the reactor was kept in an air bath at about 50 °C, well below known disproportionation temperatures,[5] until the resistance became constant. The reactor was then pumped at ambient temperatures until a constant resistance was obtained. Most of the doped $(CH)_x$ films had the golden-yellow colour characteristic of the metallic state. They were reweighed in the dry box and their compositions obtained by assuming a weight increase to be due to MF_5 uptake only.

Results are given in Table 1 for six pentafluorides together with their fluoride ion affinities, where known. There is relatively little change in the conductivities of all the doped polyacetylenes studied beyond the semiconductor-to-metal transition,[1] which occurs at about 2 mol %. Conductivities given in Table 1, therefore, can be considered to be near the maximum attainable irrespective of the exact composition once this transition has been reached. It is apparent that conductivities change inversely with the fluoride ion affinities. This could be due to partial fluorination of the host[6] or the charge localisation referred to previously.[4] One of the reactions suggested to occur upon doping with AsF_5,[7] although still subject to controversy is shown in equation (1).[7] The fact that both AsF_5 and SbF_5 give highly conducting

$$3AsF_5 + 2e \rightarrow 2AsF_6^- + AsF_3 \qquad (1)$$

polymers despite having high fluoride ion affinities suggests that a different type of chemical reaction occurs upon doping with transition metal pentafluorides.

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