The ^{31}P Resonance of PF_6^- and Related Subspecies Intercalated in Graphite as a Function of Temperature

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The intercalation of various complex fluoride ions in graphite has been studied by a number of workers.[1-3] Many of these have been concerned with the stoichiometry of the resulting complexes, i.e. the stages of the complexes formed, and to a lesser extent the effect of temperature on reorientation. Although some of the studies were carried out using NMR, they were done several years ago when high-frequency, high-powered pulse equipment was not available. Thus the results were not very informative with regard to reorientation and the possibility of multiple species being present.

As described in ref 2, Ebert and co-workers carried out both ^{19}F and ^{31}P resonance studies of the PF_6^- ion produced by the reaction of ClF, PF_5, and graphite. The stoichiometries studied were $C_{28}PF_6$ and $C_{14}PF_6$ and the temperatures were varied from −168 to +23 °C. For the second compound a variation of the chemical shift with temperature was found, suggesting that a reaction occurred at some temperature in this range. Unfortunately the resolution was not good enough to determine the chemical shifts of the various species involved but it was suggested that a PF_5/PF_6^- equilibrium occurred. In another study Miller et al.[3] examined $NOPF_6$ and found a single PF_6^- species that was static at all temperatures studied.

In the present study graphite PF_6 adduct was synthesized by reacting a 1:1 mixture of fluorine and phosphorous pentafluoride at 2.0 atm of total pressure with SP1 graphite at ambient temperature for several days. On the basis of weight increase, the stoichiometry was found to be $C_{14}PF_6$. X-ray powder spectra gave peaks at $2\theta = 22.8$ (s), 34.8 (m), 42.4 (vw), and 59.8° (m), which are interpreted as the 002, 003, 100, and 005 lines of the first stage compound with $d = 7.68$ Å. The ^{31}P resonance was observed at 121.3 MHz over a temperature range from −132 to +45° using a Bruker CXP-300 NMR pulse spectrometer. Observations were made at different temperatures starting from ambient and going down and increasing from the lowest temperature to 45 °C. In no case did the observations show any hysteresis.

The spectra recorded at −132, −90, −39, and +45 °C are shown in Figure 1. At low temperatures the spectra show the characteristic reorientation of an octahedron of the PF_6^- ion based on the relation derived by Spiess.[4] The spectrum at −39 °C differs from the normal line narrowing expected at higher temperatures by showing the P–F coupling of 700 Hz that is seen in solution, at a lower chemical shift than the main peak. An examination of the spectrum shows that at most six peaks are visible while seven would be expected for an octahedral structure of six fluorine atoms around a phosphorous atom. At −18.7 °C (not shown) a second peak appears where the P–F couplings were observed at −39 °C, and both peaks are further narrowed showing that the reciprocal of the reorientation time is at a higher frequency than the P–F couplings. At higher temperatures the peak separation between the PF_6^- and the new peak remains constant.

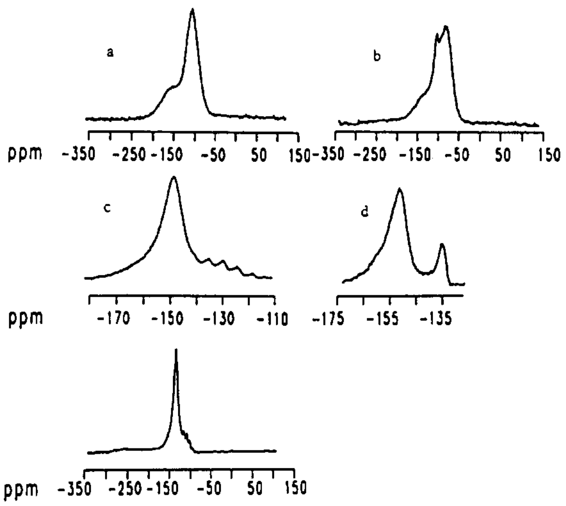

Figure 1. ^{31}P NMR spectrum of graphite–PF_6: (a) −132 °C; (b) −90 °C; (c) −39 °C; (d) +45 °C.

The chemical shift of ^{31}P in PF_6^- relative to 85% phosphoric acid is −151 ppm while that of PF_5 is −80 ppm.[2] The shift of the second peak in the present work is −131 ppm. A search of the literature showed no other ^{31}P chemical shift of a species containing fluorine in this range and so it is concluded that this substance must be new. The most reasonable formula is $P_2F_{11}^-$ since the shift would be expected to fall between PF_6^- and PF_5. Unfortunately in the present work it was not possible to obtain an ^{19}F spectrum of the sample because the probe contained a large block of tetrafluoroethylene polymer and subtractive spectra were too unreliable. Therefore it could not be determined whether more than one type of fluorine atoms were present.

An estimate of the relative amounts of each of the species present was made by measuring the areas under the peaks at several different temperatures and taking the ratios of each area to the total area at that temperature. At 45.5, 23.8, and −1.0 °C the ratios were found to be constant. This makes it very unlikely that an equilibrium of the type

$$2PF_6^- = P_2F_{11}^- + F^-$$

is occurring since it would require zero enthalpy of reaction. Presumably the formation of the second species occurs during the initial intercalation process after which all of the intercalated species remain in place. The peaks at −39 °C are due to the second substance which is reorienting at a lower rate than the P–F coupling frequency. From the fact that reorientation occurs at a much higher temperature than for PF_6^-, it is concluded that the species must be of higher molecular weight. The actual structure of this species cannot be determined without more information. Finally although there appears to be no interaction between PF_6^- and the new species, this could occur at higher temperatures. Unfortunately concern for damage to the spectrometer limited these measurements.

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