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The Solid State ^{13}C-NMR Spectra of Some Intercalation Compounds

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The ^{13}C-nuclear magnetic resonance spectra of graphite bromine (C_8Br) and two graphite potassium compounds (C_8K and $C_{24}K$) have been obtained in the solid state. A similar spectrum is observed for all three compounds. The major feature in all three compounds is a very broad upfield resonance. These spectra are interpreted as indicative of an interaction of the intercalate with the graphite π system leading to more aliphatic-like carbon atoms.

Introduction

Graphite is known to react with a variety of Lewis acids and bases to form lamellar compounds in which the planar graphite arrangement of the carbon atoms is not disturbed. Among these are graphite compounds of the alkali metal, bromine, interhalogen, metal halide, metal oxide, as well as the graphitic acid salts (*1*). To date there is no comprehensive theory as to why these materials intercalate and how they couple with the carbon atoms.

A few nuclear magnetic resonance (NMR) studies have appeared on intercalation compounds (*2–5*). Both Jensen *et al.* (*2*) and Carver (*3*) have reported data from cesium-133 and carbon-13 resonances. The cesium Knight shift indicates that cesium is partially ionized in C_8Cs and completely ionized in cesium poorer stages. A Knight shift, although small, is also observed for lithium resonance in C_6Li (*4*). Fluorine NMR studies on intercalation compounds of nonmetal fluorides have been used to determine the oxidation state of the nonmetal (*5*).

In this paper we report the solid state NMR spectra of graphite potassium and graphite bromine intercalation compounds. These include C_8K, C_8Br, and $C_{24}K$. The graphite–potassium system has been extensively studied (*6, 7*). Several stages of compounds from C_8K to $C_{60}K$ are known (*6*). Graphite bromine (C_8Br) on the other hand gives only the second-stage compound in which a bromine atom in a triangular network is intercalated between every pair of graphite layers. The C_8K compound is a first-stage structure in which a triangular net of potassium atoms is intercalated to give alternating graphite and potassium layers. A hexagonal net of potassium atoms is found in the second state structure for $C_{24}K$.

Both C_8K and $C_{24}K$ are reported to be weakly paramagnetic, while C_8Br is weakly diamagnetic (*8, 9*). Electrical and volume measurements on C_8K establish the cationic nature of the potassium while similar measurements on C_8Br indicate charge transfer from graphite to bromine (*8*). In neither case is complete ionic character indicated.

Experimental

Potassium graphite compounds were prepared by mixing the stoichiometric quantity

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of potassium with degassed graphite under high-vacuum conditions in a 10-mm NMR tube. Heating the tube for 2 days at 125°C produced the bronze gold C_8K. An authentic sample of the steel-blue C24K was obtained from Dr. T. Schaaf of the General Telephone and Telegraph Company and used directly. The graphite Br_2 compound (C_8Br) was obtained by combining the stoichiometric amount of Br_2 with degassed graphite at room temperature.

The ^{13}C-NMR spectra on powder samples were obtained using a JEOL FX-60 spectrometer operating in the external lock mode under high-resolution conditions, as previously reported (*10*). A flip angle of about 30° was used with TMS as an external reference by tube substitution. Spectra were obtained at about 30°C using either 4K or 8K data points over a spectral width of 10 000 Hz. The scan repetition rate was varied between 0.6 and 1.6 sec; spectra usually required 100 000 to 200 000 pulses.

Results and Discussion

The ^{13}C-NMR spectra of C_8Br, C_8K, and $C_{24}K$ are all surprisingly similar. The major resonance for each compound occurs at approximately 40 ppm above TMS with a second (minor) resonance well downfield at approximately 180 ppm. These spectra are shown in Fig. 1. An excess of bromine when added to the C_8Br did not alter the ^{13}C-NMR spectrum of C_8Br. The typical bandwidths at half-height are approximately 1 kHz. The spin–lattice relaxation times of the two resonances may be quite different. As a consequence the relative intensities may not be interpreted in terms of relative quantities of different bond types under the conditions that have been used to obtain these spectra.

Electronically graphite is a semimetal with a nearly filled π conduction band (*1*). Thus, one might suspect that an electron can be added or removed from this conduction band. The observed position of resonance at high field for all the compounds may simply reflect the ease of electron donation or acceptance into this band. The similarity of the resonance's position to that of diamond (*10, 11*) most likely indicates an interaction of the potassium (or bromine) with the graphite π system. This interaction will give rise to a change to more aliphatic-like carbon atoms.

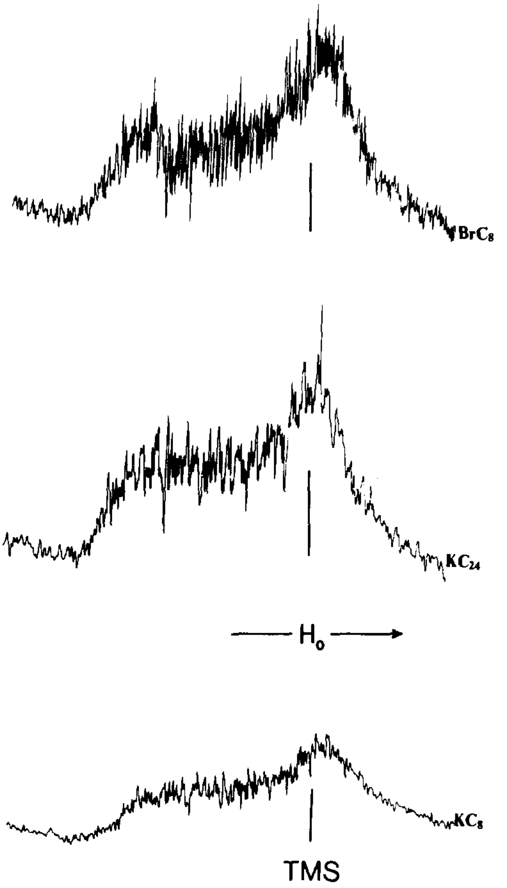

FIG. 1. ^{13}C-NMR spectra of C_8Br, $C_{24}K$, and C_8K. The total spectral width is 10 000 Hz and the major resonance is approximately 40 ppm above TMS. The field strength increases from left to right.

This interpretation is in accord with many other observations on intercalation compounds. An increase in C–C bond length, to be expected for a more aliphatic-like carbon, has been noted on going from graphite to C_8K (*12*). In addition, Ebert (*1*) has calculated that the metal atoms or ions penetrate 0.3 to 0.35 Å into the π cloud of the graphite. In a lithium-7 NMR study, evidence is presented for an interaction between lithium and the graphite π-orbitals (*4*). Finally, Fisher has stated, based upon size effects, that the p_z orbitals of the graphite are destroyed by *sp* hybridization upon interaction with donor atoms. For acceptors (e.g., Br_2) he suggests that bonding is of the Van der Waals type (*13*).

Further evidence for the difference between graphite and intercalation compounds comes from both vibrational spectra (*14–16*) and ESCA studies (*17–20*). The main feature reported in the Raman spectrum of graphite is a band at 1582 cm^{-1} which changes in intensity upon intercalation. These changes in this in-plane graphite vibration are reported to be associated with coupling between the intercalate and the graphite layers. The results of the ESCA studies also show that differences in the spectra between pure graphite and intercalation compounds are primarily those of bandwidth. The bandwidth of $C_{12}Br$ is drastically reduced on the transfer of electrons from graphite to bromine (*17*), whereas the bandwidths in plots of valence bands of C_8H and in various graphite potassium compounds are widened upon transfer of electrons from the intercalate to graphite (*17–19*). Results of low temperature specific heat experiments are in accord with the electronic structures of C_xK and C_xCs ($x = 8$, 24, 36, 48) being mainly determined by the effect of alkali metal valence electrons on the electronic structure of pure graphite (*20, 21*).

Conclusions

Investigations of intercalation compounds by diffraction techniques, vibrational spectroscopy, specific heat measurements, and ESCA studies have all indicated that the process of intercalation causes changes in the graphite which seem to involve primarily the π orbitals of the graphite. Further evidence for the interaction of the π electrons of graphite with the intercalate is given by the NMR spectra of several intercalation compounds reported herein.

Acknowledgment

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