¹³ C NMR of Intercalation Compounds of Graphite and Other Benzenoid Systems

Lawrence B. Ebert, Armando R. Garcia, and Daniel R. Mills Exxon Research and Engineering Company Annandale, NJ 08801

<u>Abstract</u>. To understand the ¹³C NMR of intercalation compounds of graphite, one can invoke analogies to several systems: metals, closed shell aromatic ions, and aromatic radical ions. To assess these alternatives, one needs to measure the T_1 and the Knight shift of the carbon resonance. Complexities can arise from intercalated paramagnets.

In the case of ions of aromatic hydrocarbons, the ¹³C NMR absorption can be broadened by exchange between closed shell species and radical ions. Species which do not exchange, such as hydrido-carbanions formed by attack by protons, can be observed, but may be a minority species. This problem may be of relevance to the proposal of "tetra-anions" of perylene and of pyrene.

Introduction

Carbon-13 NMR is useful in characterizing a wide variety of benzenoid systems, ranging from graphite to fossil fuels. In the case of intercalation compounds of graphite, the resonance position, if properly interpreted, could yield information about the extent of charge transfer between graphite host and inserted guest, an issue which has been somewhat controversial in the last ten years (1). To understand the C-13 spectra in graphite compounds, one may use several possible analogies:

1. Because the compounds have metallic conductivity, one could treat the spectra in terms of the NMR theory of metals, in which relaxation follows a Korringa Law relation $(T_1 \times T \propto (Knight shift)^{-2}$. Since both donor and acceptor compounds have greater conductivity than graphite, they should both have shifts at higher field than that of graphite, and they both should have T_1 values less than that of graphite.

2. Because graphite compounds may be viewed as charged benzenoid species, one could interpret the shifts in terms of chemical shift/charge transfer correlations worked out for closed shell ions of small aromatic hydrocarbons.

3. Because graphite compounds contain benzenoid sheets which are not only charged but also contain unpaired electrons, one might relate observed shifts to the Fermi contact term, as done for

aromatic radical ions. For these species, the shift of a given carbon atom in the benzenoid ion is related to the magnitude and sign of its hyperfine coupling constant.

4. Because graphite compounds are anisotropic, periodic solids, one might require detailed band theory to interpret the shifts (2). Herein, shifts are expressed in terms of "band" and "dipole" contributions, with donor, but not acceptor, compounds having a nonzero dipole term only because of the metallic nature of the donor compounds so far studied. The "band" term has been proposed to be independent of intercalate concentration, and presumably charge transfer (2).

Herein, we illustrate these points with data concerning C-13 NMR of graphite acceptors, the pyrene/perylene tetra-anion discussion (3), and the $C_{\rm R}$ K/H₂O discussion (4).

Results and Discussion

In terms of T_1 , $C_{24}K$ has been reported to obey the Korringa Law (5). We find that different graphite/acceptor compounds can have different T_1 behavior: samples from SP-1 graphite with intercalated paramagnets (" $C_{14}UF_6$ " or " $C_{14}CrO_3$) have the shortest T_1 's, followed by $C_{10}AsF_5$ and $C_{14}PF_6$ (which show temperature independent paramagnetism, as measured by ESR). A 91% C-13 enriched Boudouard carbon (XRD L = 120 A), when intercalated with bromine, shows relatively long T₁ values (at 298 K, T₁ = 2.1 sec at 15 MHz and 4.8 sec at 90 MHz).

In terms of shift position, we have reported that acceptor compounds made from polycrystalline SP-1 graphite have a single resonance slightly downfield from the position of benzene (1). The uniformity of results suggests a "motional averaging" process of the type reported for the ESR of polycrystalline graphites by Singer (6). Some workers have utilized chemical shift/charge transfer correlations derived for closed shell aromatic ions to infer that the small shifts observed in graphite/acceptors indicate negligible charge transfer (7). The relevance of such correlations to graphite compounds is questionable, for the correlations are based on data on small, closed-shell ions, in which the transferred charge is located on peripheral carbon atoms. When electron exchange is present, the situation is more complex, as illustrated in the recent debate over the existence of tetra-anions of pyrene and perylene (3).

After a period of weeks, one can obtain high resolution proton and carbon spectra of a mixture of pyrene, dg-THF, and alkali metal, and various workers have ascribed such spectra to the pyrene dianion, the pyrene tetra-anion, or the hydridopyrene carbanion, all of which are closed shell species. Current wisdom suggests that the last entity may be the observed species, with electron exchange between radical anion and dianion broadening the spectra of these species at room temperature. In the case of a perylene, THF, sodium metal mixture, we find that high power, wide line techniques give a C-13 spectrum with two peaks (15 MHz, 298 K). The peaks are about 0.35 G wide, are about 45 ppm apart, and are of equal intensity, indicating that they arise from the THF. No evidence for perylene species could be found. If such evidence were found, the shifts of the resonance positions would be determined by the Fermi contact term, and not by the above mentioned chemical shift/charge transfer correlations.

The tetra-anion discussion is of relevance to charge transfer issues in graphite chemistry. If one could make the pyrene tetra-anion, in which 4 electrons are distributed among 16 carbon atoms, then a formulation of $C_0^{\rm KK+}$ for the first stage graphite intercalation compound would not seem unreasonable. In the case of perylene, $C_{20}H_{12}$, we have found that one can obtain the "correct" NMR spectra after a potassium consumption of only 2 mole K/mole perylene. On quenching this solution with methyl iodide, the major product is di-methyl di-hydro perylene.

Thus, charge transfer in aromatic hydrocarbons (1 e⁻ for ten carbon atoms in the dianion of perylene) is of the same order of magnitude as in intercalation compounds. However, the graphite compounds, $C_{0}M$ (M=K, Rb, Cs), appear to have incomplete charge transfer from M⁰ to C, as shown by optical, NMR, Mossbauer, and chemical techniques. We have been interested in using the reaction of $C_{0}K$ with water as a probe of the kinetics of the anionic carbon sheets and of the electron-depleted potassium layers. We have found that the $C_{0}K/H_{2}O$ product from SP-1 graphite contains alkali metal cations with water, suggesting a kinetic limitation to the reaction of graphitic anions with protic sources.

There has been some debate about this interpretation. Schlögl and Boehm have suggested that incomplete reaction arises from topochemical limitations, and that water can react completely with C_8K as if that compound contained K^O (4). We have recently obtained data on the reaction of C_8K made from Ultracarbon UCP-325 with H_2O ;

the product contains 75.41% C, 1.12% H, and 11.64% K, as measured by Galbraith Labs. We could not remove all the potassium, even from a -325 mesh material. Furthermore, all compounds which we have studied appear to contain water, as inferred from pyrolysis/Karl-Fisher reactions. The T_1 of the protons is relatively long at room temperature (1.6 to 2.0 sec, invariant of radiofrequency) and shortees as temperature is lowered. We find that $T_1 > T_2$, as in a number of other intercalation systems.

References

- 1. L. B. Ebert, Mat. Res. Bull., <u>16</u>, 831 (1981).
- 2. T. Tsang, Sol. St. Commun., 53, 39 (1985).
- 3. B. Eliasson, Chem. Commun., p. 591 (1984).
- 4. R. Schlögl, Carbon, <u>22</u>, 351 (1984)
 - L. Ebert, Carbon, in press.
- 5. K. Kume, Synth. Met., 6, 219 (1983).
- 6. L. Singer, J. Chem. Phys., <u>37</u>, 1812 (1962).
- 7. J. Conard, Physica, 998, 521 (1980)
 - M. Suganuma, Phys. Rev. B, <u>22</u>, 5079 (1980).