Marquette University
e-Publications@Marquette

1-1-1978

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

Daniel T. Haworth
Marquette University

Charles A. Wilkie
Marquette University, charles.wilkie@marquette.edu

Contents

The solid state ^{13}C-NMR spectra of some carbides

Daniel T. Haworth
Department of Chemistry, Marquette University, Milwaukee, WI
Charles A. Wilkie
Department of Chemistry, Marquette University, Milwaukee, WI

The utility of NMR spectroscopy to the study of liquids or solids dissloved in liquids is well known. This technique has been used infrequently to studies in the solid state.[1,2] Work has been done on diamond, graphite and coal.[3-6] The ^{13}C-NMR of ebony and ivory have been studied by the magic angle technique.[7] The solid state ^{13}C-NMR spectra of graphite and diamond can be interpreted in terms of tetrahedral (sp^3)

and trigonal planar (sp^2) carbon atoms.[8] We now report our investigations using solid state ^{13}C-NMR spectroscopy to study various types of carbides.

EXPERIMENTAL

The following carbides were used as received from the supplier: CaC_2 (Fischer Scientific), Al_4C_3 (A. D. MacKay), SiC, B_4Si, $Mn_{23}C_6$ (Cerac/Pure, Inc.). The ^{13}C-NMR spectra were obtained on a JEOL FX-60 spectrometer operating in the external lock mode. A flip angle of about 300 was used. TMS was used as an external referency by tube substitution. 8 K data points were collected over a sweepwidth of 10,000 Hz. On the average, 100,000 to 150,000 pulses were required to obtain the spectra. Metal analysis were done gravimetrically using metal oxides as the weighing form. Carbon analyses in CaC_2 was done by hydrolysis followed by acid treatment of the residue. The residue was presumed to be graphite. The spectra were integrated by cutting and weighing xerox copies of the spectra. An approximately symmetrical band shape was assured.

DISCUSSION

The different structural types of carbides used in this study were: ionic, CaC_2 and Al_4C_3; interstitial, $Mn_{23}C_6$ and covalent, SiC and B_4C. Calcium carbide structure consists of discrete Ca^{2+} and C_2^{2-} ions in the lattice structure, whereas Al_4C_3 has carbon atoms (methanides) in its structure.[9] The interstitial carbide, $Mn_{23}C_6$ has cubic symmetry with four formula units per unit cell.[10] It is ismorphous with $Cr_{23}C_6$ and is an important constituent in strengthening steels.[11] Silicon carbide has a diamond structure with each carbon atom tetrahedrally bonded to four silicon atoms and each silicon atom is bonded to four carbon atoms.[9] Boron carbide has a "NaCl" structure with four covalently bonded icosahedron of borons (B_{12}) and four carbon atoms per unit cell. The carbon atoms occur in linear chains of groups of three which are covalently bonded to the boron atoms in different icosahedra.[9] The carbon in both Al_4C_3 and SiC is certainly tetrahedral and thus the chemical shift is expected near TMS. The carbon in CaC_2 is acetylenic which is normally a little downfield from TMS. Both $Mn_{23}C_6$ and B_4C also no doubt contain non-aromatic carbon atoms and these resonances are expected in the approximate region of TMS.

The ^{13}C-NMR spectra of CaC_2, $Mn_{23}C_6$ and SiC are shown in Fig. 1. One notes that all of the resonances are very broad with half width of about 1000Hz. The spectra of CaC_2 show two carbon resonances at approx. 167ppm (minor) and -72ppm (major). The minor downfield resonance has approximately the chemical shift of graphite and is thus tentatively assigned to a graphite impurity in the CaC_2. The high field resonance is in a region where non-aromatic carbons are expected and is assigned as the carbide carbon. Approximate integration of these very broad resonances yield a ratio of 15:85 (±15) for the low field to high field resonances. This indicates a graphite impurity of 3-7% in the CaC_2. Graphite analysis (done by reaction with dilute HCl and followed by extensive washing to leave only graphite), indicates that about 6% graphite is present in this sample of CaC_2. Calcium analysis (62.66% Ca), indicates that some of the calcium occurs as CaO. The synthesis of a sample of CaC_2 in a state of high purity is very difficult as has been reported by Flowers *et al.*[14]
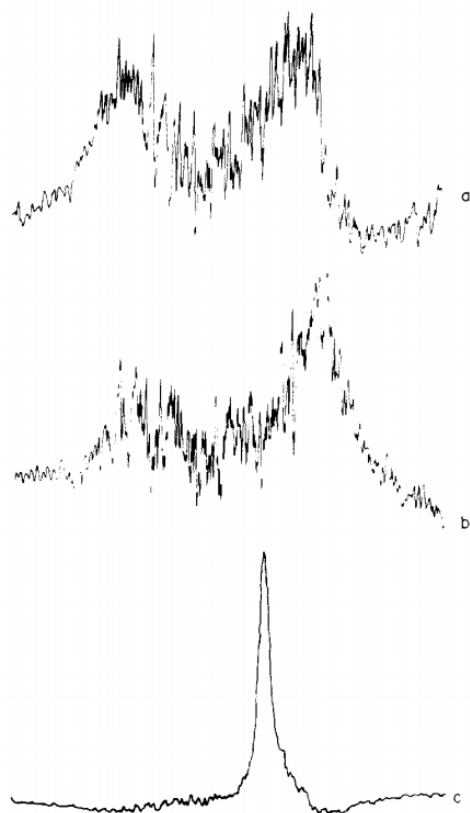
Fig. 1. Solid state ^{13}C-NMR spectra of CaC_2 (a) $Mn_{23}C_6$ (b) and SiC (c) over a 10,000 Hz sweepwidth.

The spectrum of $Mn_{23}C_6$ also shows two peaks at about 178ppm (minor) and -64ppm (major). Silicon carbide shows only one resonance at approx. 21 ppm. Table 1 summarizes the chemical shifts for the carbide compounds examined and it also includes the ^{13}C-NMR chemical shift data for graphite and diamond.[8] The carbon resonance in diamond ($\sim$- 45 ppm) is within the range of the high field resonance observed in the carbides, Thus, one concludes that similar types of carbons are present in the high field resonance of SiC and $Mn_{23}C_6$. This is consistent with the observed structure of these carbides. The carbon--carbon distance in calcium carbide is 1.19 Å as compared to 1.20 Å in acetylene.[12] The ^{13}C-chemical shift of acetylene is ~70ppm from TMS.[13] The high field resonance in CaC_2 is assigned to the acetylide ion and the negative charge on the carbide ion should produce an upfield shift (-72 ppm).

The methanide carbon atoms in Al_4C_3 occur singlely and the ^{13}C-data for these carbons suggest that they have aliphatic character (sp^3). The boron carbide carbons are covalently bonded and its spectra gives a resonance in the aliphatic region. Similarly, the chains of carbon atoms in the interstitial carbide, $Mn_{23}C_6$, are also of the aliphatic type. Integration yields the low field to high field resonance ratio as 15:85 (-+ 15). This indicates about a 3% graphite impurity by NMR measurement. Chemical analysis gives 57.78% aluminum which indicates that Al_4C_3 contains 20-30% Al_4C_3, about 3% graphite and the balance being Al_2O_3.

Table 1. ^{13}C-NMR chemical shift data for various carbides

Compound	Low Field Resonance[*]	High Field Resonance[*]
CaC_2	~ 167	~ -72
Al_4C_3	~ 200	~ -52
B_4C	~ 191	~ -66
SiC		~ 21
$Mn_{23}C_6$	~ 178	~ -64
Graphite	~ 155	
Diamond		~ -45

[*] ppm from TMS

The B_4C was analyzed by Cerac as 74% boron and 24% carbon. Using the method of triangulation, this sample of B4C would correspond to 96% B4C. Of the 24% carbon, 3% would constitute a graphite impurity. This is comparable to the 4% graphite impurity obtained by integration.

Perhaps the more interesting spectra is that of SiC. This was recorded after only 25,000 pulses and it shows only one carbon resonance at about 21 ppm. The single resonance indicates no graphite impurity and this is in agreement with the analysis of this lot of SiC as being $Si_{1.00}C_{1.01}$ with traces of several metals. The high signal to noise ratio is difficult to explain. Perhaps the motional characteristics for SiC are very different from the other carbides producing the high SIN ratio. Silicon carbide and diamond have the same structure yet the chemical shift of SiC is about 65 ppm downfield from the diamond carbon resonance. This deshielding of carbon in SiC is not easily explained in terms of a simple molecular orbital diagram for a carbon atom tetrahedrally surrounded by four silicon atoms, but one would have to consider this deshielding in terms of band theory (perhaps a Si-Si interaction) or a force field of an array of silicon and carbon nuclei.[15]

Acknowledgement

References

1. M. Mehring, NMR: *Basic Principles and Progress* (Edited by P. Diehl, E. F-uck and R. Kosfeld), Vol. 11. Springer Verlag, New York (1976).
2. *Nuclear Magnetic Resonance in Solids* (Edited by L. Van C, erven). Plenum Press, New York (1977).
3. H. L. Retcofsky and R. A. Friedel, *Anal. Chem*. **43**, 485 (1971).
4. H. L. Retcofsky and R. A. Friedel, *J. Phys. Chem*. **77**, 68 (1973).
5. D. L. VanderHart and H. L. Retcofsky, *Fuel* **55**, 202 (1976).
6. H. L. Retcofsky, *Appl. Spectrosc*. **31**,116 (1977).
7. J. Schaefer and E. O. Stejskal, *J. Am. Chem. Soc*. **98**, 1031 (1976).
9. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 3rd Edn, p. 290. Wiley-lnterscience, New York (1972).
I0. A. H. Sully, *Manganese-Metallurgy of the Rarer Metals*-3, p. 259. Academic Press, New York (1955).
II. L. E. Toth, *Transition Metal Carbides and Nitrides*, Refractory Materials (Edited by J. A. Margrave) Vol. 7, Chap. I. Academic Press, New York (1971).
12. J. J. Lagawski, *Modem Inorganic Chemistry*, p. 340. Marcel Dekker, New York (1973).
13. L B. Stothers, Carbon-13 NMR *Spectroscopy*, p. 118. Academic Press, New York (1972).

14. R. L. Faircloth, R. H. Flowers and F. C. W. Pummery, *J. Inorg. NucL Chem*. **29**, 311 (1967).
15. J. L. T. Waugh, *The Constitution of Inorganic Compounds*, Part M, M. 5. Wiley-Interscience, New York (1972).