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Charles A. Wilkie

Marquette University, charles.wilkie@marquette.edu

Daniel T. Haworth

Marquette University

Marquette University

e-Publications@Marquette

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THE ^{13}C -NMR SOLID STATE SPECTROSCOPY OF VARIOUS CLASSES OF COALS

Charles A. Wilkie

Department of Chemistry, Marquette University, Milwaukee, WI

Daniel T. Haworth

Department of Chemistry, Marquette University, Milwaukee, WI

Abstract

The ^{13}C -NMR spectra of various classes of coal obtained in the solid state show two resonances, one of which is assigned to aromatic carbon and the other to aliphatic carbon. The resonances are very broad with the high field resonance centered at about 7 ppm below tetramethylsilane and a low field resonance centered at about 140 ppm below tetramethylsilane. Based on our previous solid state ^{13}C -NMR studies of graphite and diamond, the high field resonance is typical of a sp^3 carbon whereas the low field resonance is assigned to a sp^2 carbon whereas the low field resonance is assigned to a sp^2 carbon. It is found that the antracitic coals have more aromatic (sp^2) carbons than the bituminous, subbituminous and lignite coals. The analytical implications of this technique are briefly discussed.

INTRODUCTION

The ^{13}C -NMR spectra of various classes of coals have been examined both as solids and as soluble extracts. VanderHart and Retcofsky¹ have observed two resonances which they have assigned to the aromatic and aliphatic components of the coals. Carbon disulfide extracts of coals² have also revealed both aromatic and aliphatic components. Earlier work showed only one carbon resonance in coal.^{3,4} Very recent work^{5,6} has utilized cross-polarization⁷ and magic angle spinning.⁸ There is a time saving from the crosspolarization experiment and significant resolution enhancement from the magic angle experiment.

We have recently reported our NMR studies on graphite and diamond⁹ as well as on metal carbides.¹⁰ The work on metal carbides demonstrated that quantitative analysis of the various components was possible by this technique. In this paper we report our results on ^{13}C -NMR spectroscopy of coals of various ranks.

EXPERIMENTAL

The ^{13}C -NMR spectra were taken on a JOEL FX-60 spectrometer operating in the external lock mode. A flip angle of 30° was used. TMS was used on an external reference by tube substitution. 8K data points were collected over a sweep width of 10,000Hz. Approximately 100,000-150,000 pulses were usually accumulated.

All of the coal samples were obtained through the Coal Research Section at the Pennsylvania State University (PSOC). Coal samples were packed into a 10 mm NMR tube and spectra obtained directly

RESULTS AND DISCUSSIONS

Spectra have previously been reported for several of the classes of coal. In this study we have examined anthracite, bituminous, subbituminous and lignite allowing a comparison among these coals. Table 1 summarizes the various types of coal used in this study as well as some analytical data. Figures 1 and 2 gives typical ^{13}C -NMR for the coals examined. The half width of all the resonances are very broad and in excess of 1,000Hz. Examination of the spectra of the coals show that bituminous, subbituminous and lignite coals all gave two resonances in about the same intensity ratio (Fig. 1). The low field resonance occurs at about 140 ppm below TMS and this absorption is assigned to the aromatic (sp^2 type) carbon resonance. A high field absorption centered at about 5 ppm above TMS is assigned to an aliphatic (sp^3 type) carbon resonance. As pointed out by Vander Hart and Retcofsky¹ it is quite simplistic to assign

these resonances to aromatic and aliphatic carbons, respectively. There are certainly other contributors to each of the resonances. The chemical shift anisotropy of the aromatic resonance gives rise to a very long tail which extends down close to or perhaps partially overlapping with the aliphatic resonance. It is thus quite difficult to even semiquantitatively integrate these resonances to obtain relative amounts. Maciel *et al.*⁵ have shown by a comparison of a magic angle spectrum with the normal spectrum that the error is significant and it depends on the relative amounts of aromatic to aliphatic carbons. Spinning is important to quantify a highly aromatic coal. The magic angle technique removes the anisotropy giving two relatively separate and integratable resonances.

The spin lattice relaxation behavior of all these coals is unknown, but it seems reasonable to assume essentially similar relaxation times in all the coals. The relaxation times for the various components may also be different, this presents a substantial difficulty in the accurate determination of the ratio of aliphatic to aromatic carbons.

The coals of the anthracite class (No. 80 and 84) also show two resonances; however, the low field resonance (aromatic) is clearly dominate in this coal (Fig. 2). The spectrum is quite similar to that reported by Maciel.⁵ These resonances occur at approximately the same chemical shifts (140 ppm and 7 ppm) as those resonances of the nonanthracitic coals. Clearly, these anthracitic coals contain more aromatic carbon than the other classes of coals. While the spectra of the anthracitic coals show a large aromatic to aliphatic ratio, the spectra of the subbituminous coals show two resonances in about equal intensity. The subbituminous coals show the aliphatic resonance to be slightly larger than the aromatic resonance and the lignite resonance shows more distortion in favor of the aliphatic carbon resonance. One cannot quantify these resonances in terms of aromaticity as explained above.

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Table I. Classification of coals by rank used in the ¹³C-NMR study

Class	Group	(PSOC No.)	% Carbon (Dry Basis)	% Volatile	Clorific Value (BTU/lb)
Anthracitic	Anthracite	(80)	92.37	5.77	12,603
	Semi-anthracite	(84)	92.90	8.28	11,194
Bituminous	Low-Volatile	(119)	88.02	15.22	8,201
	Medium-Volatile	(132)	91.05	22.02	15,177
	High-Volatile	(284)	85.69	38.39	11,597
Subbituminous	A	(248)	75.62	43.50	12,661
	B	(240)	74.86	39.12	9,952
	C	(139)	73.73	43.08	10,576
Lignite	Lignite	(246)	71.88	44.73	10,596

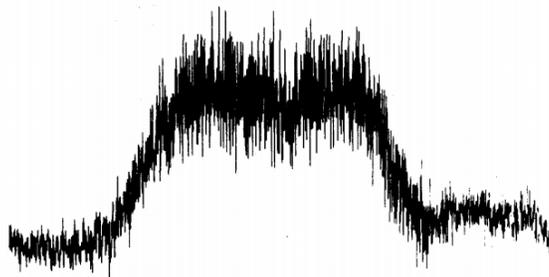


Fig. 1. ^{13}C -NMR solid state spectrum of a sample of subbituminous coal, group B PSOC No. 240 over a 10,000 Hz sweepwidth (665 ppm), peaks are approx. 140 ppm and -7 ppm from TMS.

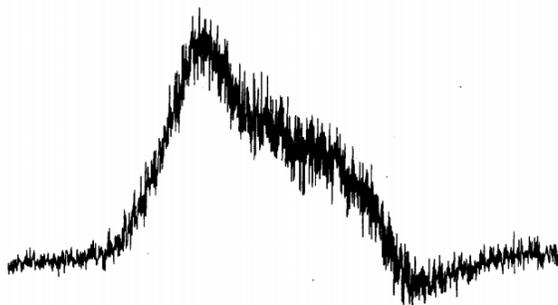


Fig. 2. ^{13}C -NMR solid state spectrum of a sample of anthracite coal, PSOC No. 80 over a 10,000 Hz sweepwidth (665 ppm), peaks are approx. 140 ppm and -7 ppm from TMS.

It is also interesting to note that the ^{13}C -NMR spectra of the anthracite coals required only about 50,000 pulses to obtain a better signal to noise ratio. A higher signal to noise ratio was also observed in the spectrum of silicon carbide.¹⁰ Presumably this phenomenon is the result of a more highly ordered structure of the carbon atoms in the anthracite coals than in the other classes of coals examined. An alternate explanation is that in the majority of samples that we have examined the samples themselves cause some probe detuning, this then requires a large number of pulses compared to a sample such as anthracite or silicon carbide for which, for unknown reasons, the detuning is not as severe. There are some indications that this latter reason is, in fact, the explanation; however, the matter is currently being pursued.

The ^{13}C -NMR spectra of lignite (No. 246) and anthracite (No. 80) were also obtained without proton decoupling. There is no difference between the completely, noise decoupled spectrum and the spectrum with the decoupler off. The line width is determined by the dipolar coupling which is not affected by the relatively weak decoupling fields that have been used in these investigations.

The spectra of anthracite and lignite obtained by Maciel *et al.*⁵ may be compared with those reported herein. The two spectra of the anthracite coals are remarkably similar while the lignite spectra appear a little different; yet the relative intensities are approximately the same. Maciel's spectra were obtained by crosspolarization which makes use of the hydrogen in the sample to transfer magnetization to the carbons. This circumvents the problem of the long spin-lattice relaxation times; it does however create a new problem, carbons isolated from hydrogen will not be crosspolarized and therefore may not be detected in the experiment. This is possible in a condensed polyaromatic region within coal.⁵ Under the experimental conditions described herein all carbons will be detected; however, due to the short pulse delay time combined with the presumed long relaxation time absolute intensities may not be meaningful.

CONCLUSIONS

The ^{13}C -NMR experiment may be used to distinguish between the aromatic-type and aliphatic-type carbons atoms in various classes of coal. There is apparently little difference in spectra obtained using "normal" techniques and those obtained from cross-polarization experiments. The cross-polarization technique offers a substantial savings in time (20-30 min⁵ vs 8-10hr) over the "normal" technique. Cross-polarization is a more difficult experiment; however, which to some extent mitigates this time savings. The magic angle technique with dipolar decoupling and more rapid magic angle spinning to separate isotropic shifts clearly offers a superior approach to coal structure. Spinning is less important in experiments designed to measure the aromatic to aliphatic carbons when the aliphatic carbons are predominant.⁵

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