Solid-State $^{13}$C and $^1$H NMR in Kerogen Research: Uncertainty of Aromaticity Estimation

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INTRODUCTION

There is currently interest in the chemical characterization of kerogens, primarily for better understanding of the origin, chemical history, and classifications of these materials. Recently developed methods for obtaining high-resolution $^{13}$C and $^1$H NMR spectra of solids have been exploited in structural characterization of kerogens.\(^1\) In particular, $^{13}$C CP/MAS spectroscopy has been extensively used in coal and kerogen studies to determine the aromatic/alkenic (or $sp^2$-hybridized) fraction ($f_a$) of total carbon that comprises aromatic/alkenic structures.\(^3\) Such calculations are based on the integrated intensities of the aromatic/alkenic and aliphatic envelopes of $^{13}$C NMR spectra.

Structural deductions based on solid-state NMR measurements, however, require that these data be correlative with other geochemical results. In particular, recent investigations in this laboratory have shown that the estimation of $f_a$ for low-rank bituminous coals based on $^{13}$C NMR contradicts elemental data.\(^4\) The purpose of the present article is to alert organic geochemists and kerogen investigators to the contradiction between $^{13}$C and $^1$H NMR date of kerogen which may adversely affect structural deductions.

DISCUSSION

In Fig. 1 are shown $^{13}$C CP/MAS NMR spectra of Green River (a), Messel (b), and Aleksinac (c) kerogens. The samples were dry powders obtained after digestion of the ground shale specimen with hydrofluoric (HF)/hydrochloric acid (HCl) (1:1 v/v) and extraction with benzene/methanol (3:1 v/v) solution. The instrumental systems for obtaining the $^{13}$C CP/MAS\(^5\) and $^1$H MAS\(^6\) NMR spectra are described elsewhere.

The spectrum of the Green River kerogen (GRK) shows two major peaks centered at 24 and 125 ppm. All chemical shifts are given relative to tetramethylsilane (TMS). The signal widths are, respectively, ~20 and 40 ppm. Similar spectra have been obtained from coals,\(^2\) coal mac-

erals,\(^8\) and carbonaceous shales.\(^9\) In these later spectra the features located over the −20 to 80 ppm range have been interpreted as arising from the aliphatic (or $sp^2$-hybridized) carbons, and the down-field features appearing between 80 and 160 ppm as arising from aromatic/alkenic carbons. GRK clearly contains carbon of both general types; accordingly, an $f_a$ value of 0.3 can be

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{$^{13}$C NMR spectrum of a kerogen sample of: (a) GRK, (b) MK, and (c) AK.}
\end{figure}

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calculated from the spectrum of Fig. 1a. It is believed that the widths of these features are mainly a consequence of the structural complexity of kerogens. The narrow linewidth in the aliphatic region indicates a homogeneity of the aliphatic species consistent with relatively large aliphatic polycyclic and/or chain structures. The somewhat broader aromatic/alkenic band, lacking an unusually sharp feature at the chemical shift of large polycyclic aromatic structures (about 120 ppm), suggests that relatively small polyaromatic ring systems characterize the aromatic portion of GRK.

The spectra of the Messel and Aleksinand shale kerogens (MK and AK, respectively) are similar to that of GRK (Fig. 1, b and c) and afford little basis for differentiating between these two materials. The peaks are centered at 30 and 130 (MK) and 22 and 115 ppm (AK) with the half-height widths similar to those of GRK [i.e., ~20 ppm (aliphatic signal) and 40 ppm (aromatic/alkenic carbon)]. The fractional contribution of aromatic/alkenic carbon to the spectra is approximately 0.5, implying that about 50% of total carbon can be attributed to aromatic/alkenic structures, within these kerogens.

Application of MAS NMR to coals has resulted in high-resolution $^1$H spectra of solid fossil fuels, and resonances at 1–3 and 6–8 ppm (from TMS) have been observed for coals and related carbonaceous materials. The 1–3 ppm resonance is attributed to aliphatic and 6–8 ppm resonance to aromatic/alkenic protons. For comparison, $^1$H MAS NMR spectra of kerogens studied are shown in Fig. 2. Surprisingly, the aromatic/alkenic feature is quite pronounced relative to that in the aliphatic region; i.e., the ratio of aliphatic proton to aromatic/alkenic proton in these carbons appears to be quite large (19, see Fig. 2), implying that about 5% of all the protons are associated with aromatic/alkenic structures.

Questions of chemical structure in GRK have received a great deal of study. Attention is called to the classic work of Yen. On the basis of combined chemical and physical studies, Yen proposed a conceptual model of the GRK, and came to the conclusion that aromatic/alkenic systems in this material either are absent or are present in minute quantities. For MK, as well as AK, the aromatic/alkenic structures are minor components. If this minor-aromatic/alkenic concept is correct, the only two reasonable explanations for the contradiction (between C and $^1$H NMR of kerogens in question) are: (1) The aromatic/alkenic structures are extensively substituted (e.g., by oxygen and nitrogen); there is, however, no persuasive geochemical evidence for this. (2) The $^13$C spectra are biased toward aromatic/alkenic features. Thus, the differences between the $^13$C CP/MAS and $^1$H MAS NMR spectra (as well as organogeochemical data) obtained for these kerogens imply that the CP/MAS $^13$C NMR spectral intensities are not representative of all the carbons in the kerogen sample and tend to overestimate aromatic/alkenic carbon. The authors hasten to point out here that we do not imply that $^1$H MAS is more reliable than $^13$C CP/MAS NMR for kerogen study, but that there is a strong disagreement between these two methods and, at the moment, it is not easy to invent an ad hoc explanation for this difference.

Microscopic examination of three kerogen samples reveals that exinite is the major (>70%) maceral type present. On the other hand, our recent study of the exinite concentrates of low-rank bituminous coals indicates that the structural data (including $f_0$) obtained through $^13$C CP/MAS NMR analysis of these materials conflict with their elemental data. Thus NMR and other geo-
chemical results imply that solid-state $^{13}$C NMR is not a reliable tool for, at least, structural characterization of exinite-rich low-rank coals and kerogens.