^{13}C NMR ANALYSIS OF MODEL SULFONIUM SALTS

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INTRODUCTION

The speciation and quantification of organic sulfur forms in fossil fuels is an area of research which has received much attention in recent years (1). Most of the techniques employed either chemically change the sulfur structures or fail to fully detect sulfur structures due to their nonvolatility. Exceptions are X-ray absorption spectroscopy (XAS) and X-ray absorption near edge spectroscopy (XANES) used recently by Gorbaty et al. to quantify sulfur forms in coals and heavy petroleum (2,3). This paper describes a new, nondestructive NMR method which offers potential for identifying and quantifying sulfur forms in fossil fuels. The method is based on the methylation of sulfur compounds to form sulfonium salts. We demonstrate that the ^{13}C chemical shift of the added methyl carbon is very sensitive to the nature of the sulfur atom to which it is bonded. Thus, in principle, dialkylsulfides, alkylarylsulfides, diarylsulfides, benzothiophenes and dibenzothiophenes can be distinguished by this technique. A preliminary study using crude petroleum is presented to illustrate the potential of this technique for identifying sulfur compounds in fossil fuels.

EXPERIMENTAL

Methylation of Model Compounds

The procedure for methylation is similar to that given by Acheson and Harrison (4). Approximately 1 mmol of the sulfur compound and 1.2. mmol of $AgBF_4$ were dissolved and stirred in 3.0 mL of dichloroethane under argon. Methyl iodide (2.0 mmol) was added via syringe to the stirred solution. A yellow precipitate (AgI) immediately formed in all cases. The reaction was allowed to stir overnight after which the solution was filtered to remove AgI. The AgI precipitate was washed with acetonitrile. The filtrate was then rotovaporized at 40-50 °C to remove excess solvent. The residue was triturated with ether to give a precipitate. In some cases an oil formed which could not be precipitated, in which case the oil was dissolved in d_3-acetonitrile or d_6-acetone and analyzed directly by NMR. If a precipitate formed, it was filtered and washed with ten drops of water to remove excess $AgBF_4$. The solid was then dissolved in acetonitrile. Ether was then added until the solution became slightly turbid. The solution was then cooled in dry ice/acetone to effect crystallization. The yields ranged from 40 to 80%.

Methylation of Crude Petroleum

The same basic procedure was used to effect methylation of an Arabian crude petroleum sample. The sample was obtained from Ashland Oil and contains 2.8% sulfur. The amounts of the reagents were the same except that 1 g of petroleum was used in place of the sulfur compound. The solution was stirred overnight and then the AgI was filtered off. The solvents were removed by rotovaporization at 40-50°C and the residue was then placed in a vacuum oven overnight at room temperature. A small amount of residue (100 mg) was then dissolved in about 1 mL of d_3-acetonitrile. Not all of the residue dissolved so the solution was filtered and then placed in an NMR tube for analysis.

FT-NMR Analysis

^{13}C spectra were obtained at 270 MHz using a JEOL CPF 270 FT-NMR. A pulse width of 2.8 us and a pulse delay of 3.0 sec were used. The number of transients ranged from 1500-5000 for the petroleum samples, depending on the concentration.

RESULTS AND DISCUSSION

Model Compounds

Sulfur is an excellent nucleophile. As such, sulfides and thiophenes react with alkyl iodide to yield sulfonium ions as shown below (5,6).

$$RSR + R'I \text{ --------> } R_2R'S^+ \; I^-$$

The reaction is favored by polar solvents such as acetonitrile and acetone. Since iodide is also a good nucleophile, the reaction is reversible. However, if the reaction is carried out in the presence of silver tetrafluoroborate ($AgBF_4$), silver iodide is precipitated, leaving the poor nucleophile tetrafluoroborate as the solute anion. Alkyl and aryl sulfides and thiophenes have all been successfully alkylated by this method.

Only limited ^{13}C chemical shift information exists on methyl sulfonium salts (7,8) Therefore, we prepared models for examination by NMR spectroscopy. The results are shown in Table I, where the chemical shifts of the added methyl carbon (relative to TMS) are listed.

The S-CH_3 chemical shifts cover a 15 ppm range for the model compounds examined. Among the sulfides, the chemical shift increases with the number of aryl groups bonded to the sulfur atom. This same trend is observed for the thiophenes, with the chemical shift increasing with increased aryl substitution about the central thiophenium ring. Comparing the chemical shifts of the S-methylbenzo[b]naphtho[2,1d]thiophenium (7) and S-methyldibenzothiophenium cations (6) reveals the effect of an additional fused ring - a slight upfield shift. Although more model compound work is required, these initial results indicate the potential for speciation of sulfur forms by the NMR technique.

Methylation of Crude Petroleum

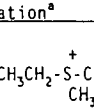
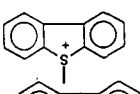
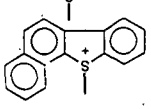
To demonstrate the usefulness of this approach, we have methylated an Arabian crude petroleum sample. The aliphatic region of the ^{13}C NMR spectrum of the crude dissolved in $CDCl_3$ is shown in Figure 1 (spectrum A). The major peak in the spectrum is at approximately 30 ppm (relative to TMS). This peak is attributed to aliphatic methylene groups by distortionless enhanced polarization transfer techniques (DEPT). The spectrum of the product from S-methylation using ordinary methyl iodide as methylating reagent is shown above this spectrum (spectrum B). The solvent is this case was d_3-acetonitrile. This spectrum is very similar to that of the original crude, with the same set of major peaks. The small differences in chemical shifts might be attributed to a solvent effect. There is no apparent evidence of added methyl groups in the spectra of the methylated crude.

The spectrum of the product using 99% ^{13}C-enriched methyl iodide is also shown in Figure 1 (spectrum C). This spectrum is strikingly different than the other two spectra. The difference is most logically attributed to added methyl groups whose signals are enhanced due to the isotopic enrichment of the methyl iodide. This spectrum is expanded in Figure 2 to illustrate more detail. Although complex, this spectrum was highly reproducible in a duplicate run. Some of the peaks can be attributed to the original petroleum and are indicated with an asterisk (*).

Obviously, the spectrum in Figure 2 contains a considerable amount of information most of which is presently not interpretable. However, some preliminary assignments can be made. The region from 32.0 to 36.0 ppm is expanded and shown in Figure 3. There are six major peaks in this region with only one peak at 32.7 attributed to the original petroleum. In order to make possible assignments for these peaks, we have spiked the sample with known samples of S-methyldibenzothiophenium and S-methylbenzo[b]naphtho[1,2d]thiophenium tetrafluoroborate salts (compounds 6 and 7, Table I, respectively). The spectrum of the spiked sample is shown above the unspiked sample. The peaks at 34.9 and 34.2 ppm are seen to grow, indicating that these peaks correspond to compounds 6 and 7, respectively. Thus a tentative assignment can be made to these two peaks in the spectrum.

TABLE I

NMR Data on Model Sulfonium Salts

Cation[a]	δ, ppm (CH_3)[b]
(1) CH_3CH_2-$\overset{+}{S}$(CH$_3$)-CH_2CH_3	21.0, 19.8[c]
(2)	25.0
(3) 	28.4
(4)	28.3
(5)	31.7
(6) 	34.9
(7) 	34.2

[a] Tetrafluoroborate salts
[b] Relative to TMS
[c] Reference 7

CONCLUSIONS

We have determined the S-CH_3 ^{13}C chemical shifts for a variety model sulfonium salts. The data reveal that the chemical shift is very sensitive to the nature of the sulfur atom bonded to the methyl group. Thus a variety of model sulfur compounds can be readily distinguished by S-methylation with subsequent NMR analysis. The ^{13}C NMR spectrum of methylated crude petroleum using isotopically-enriched methyl iodide reveals a number of peaks, most of which are unidentified at this time. More model compound work is obviously needed in order to more fully interpret the spectrum. However, it is clear that the technique offers potential for speciation of sulfur forms in fossil fuels. The technique might be particularly useful for analyzing sulfur forms in coals, since many of the sulfur-containing compounds are nonvolatile and are not readily analyzed by other techniques.

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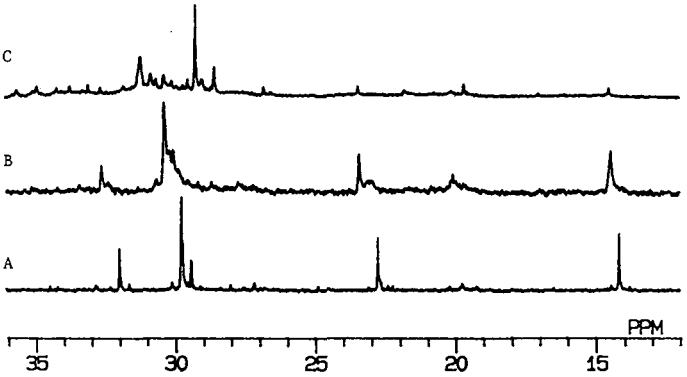

Figure 1. ^{13}C NMR Spectra of Arabian Crude. A - original crude in $CDCl_3$. B - methylated crude in d_3-acetonitrile. C - methylated crude in d_3-acetonitrile using 99% ^{13}C-enriched methyl iodide.

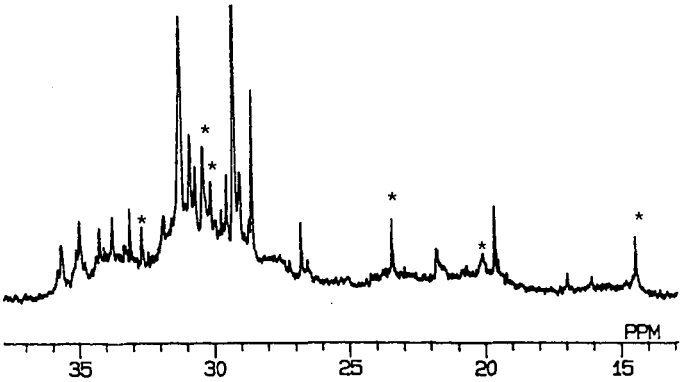

Figure 2. ^{13}C NMR Spectrum of Methylated Arabian Crude using 99% ^{13}C-enriched methyl iodide. Asterick indicates peak attributed to original crude.

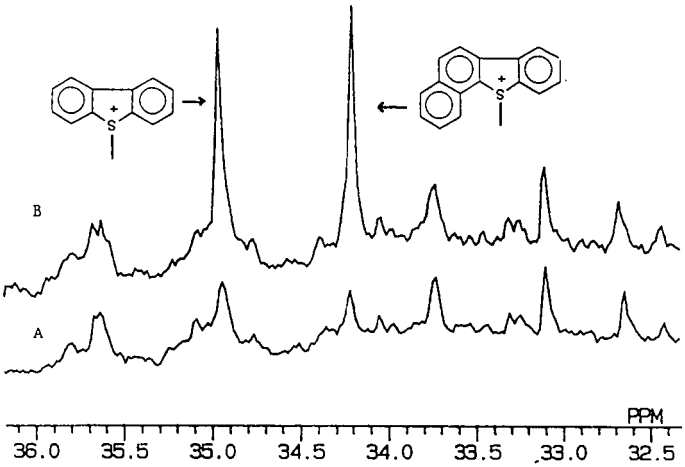

Figure 3. ^{13}C NMR Spectrum of Methylated Arabian Crude using 99% ^{13}C-enriched methyl iodide. A - unspiked sample. B - sample spiked with Compounds 6 and 7.