

ISOTOPE ANALYSES OF COMPOUNDS PRODUCED FROM CARBONIZATION OF ^{13}C LABELED 4-METHYLDIBENZOTHIOPHENE WITH FCC DECANT OILS

T. R. Filley, R. M. Filley*, S. Eser* and K. H. Freeman
Department of Geosciences

* Department of Materials Science and Engineering.
The Pennsylvania State University, University Park, PA 16802 USA

Introduction

The study of the thermal reactivities of individual compounds within complex mixtures presents a particularly challenging and potentially profitable pursuit for petroleum processing. For example, it has been shown that the molecular composition of coker feedstocks controls mesophase development, and, thus, the optical texture of the resulting cokes [1]. In particular, methyl and methylene groups on aromatic rings play an important role in controlling the reactivity of aromatic compounds and their growth into mesogens during carbonization [2-5]. Tracking the reactions of individual compounds during carbonization of coker feedstocks can shed more light on the molecular chemistry of carbonization and mesophase development.

A ^{13}C -labeled compound can be accurately tracked during its thermal alteration within an oil mixture by using, ^{13}C NMR, structural mass spectrometry, and isotope-ratio-monitoring gas chromatography mass-spectrometry (irmGCMS) [1,6,7].

In this report we present data from the irmGCMS analysis of the GC-amenable carbonization products of three Fluid Catalytic Cracking decant oils (FCC DO A, B, and C) doped with 4-methyldibenzothiophene (4-MDBT), 100% ^{13}C -labeled at the methyl substituent. Concentrations and isotopic compositions of individual aromatic components were measured to document the reaction between aromatic compounds present within the FCC and ^{13}C -enriched methyl radicals formed by thermolysis of the methyl group from ^{13}C -labeled 4-MDBT. A particular advantage of using irmGCMS is the capability to monitor the changing chemistry of individual compounds beyond the information on their net "production" or "consumption".

Experimental

Three FCC decant oils (DO A, B and C) were carbonized (500 °C) in closed tubing bomb reactors with 2 wt % 4-methyldibenzothiophene, ^{13}C -labeled 100 % at the methyl substituent. The molecular, bulk, and

elemental constitution of DO A, DO B and DO C have been discussed in detail along with the carbonization experimental conditions. The stable-carbon isotopic composition of individual GC-amenable compounds within the decant oils and carbonization product maltenes (hexane solubles) were obtained by irmGCMS as described in Filley et al. [7] for the analysis of DO A. Reported isotopic compositions are referenced to an international standard, Pee Dee Belemnite (PDB), with an $^{13}\text{C}/^{12}\text{C}$ ratio (R_{std}) of 0.011237. The isotopic compositions are reported in delta ($\delta^{13}\text{C}$) notation as described in the following equation.

$$\delta^{13}\text{C}(\text{‰}) = [(R_{\text{sa}} - R_{\text{st}}) / R_{\text{st}}] \times 1000$$

Coelution was a problem for a number of peaks, and in many circumstances individual isotopic compositions are reported for groups of two or three peaks. Reproducibility in analyses was typically better than 0.5 ‰. The following equation was used to calculate the ^{13}C enrichment ($\Delta\delta^{13}\text{C}$) with time of the methyl substituents on the aromatic ring.

$$\Delta\delta^{13}\text{C}_m (\text{‰}) = N_{\text{mp}}(\delta^{13}\text{C}_{\text{mPL}} - \delta^{13}\text{C}_{\text{mPU}})$$

where $\Delta\delta^{13}\text{C}_m$ is the calculated ^{13}C enrichment due to the labeled methyl carbons, $\delta^{13}\text{C}_{\text{mPL}}$ is the measured isotopic composition of the methyl-substituted PAH molecule in the labeled experiment, $\delta^{13}\text{C}_{\text{mPU}}$ is the measured isotopic composition of the methyl substituted PAH molecule in the unlabeled experiment, and N_{mp} the number of carbon atoms in the methyl substituted PAH. A larger $\Delta\delta^{13}\text{C}$ indicates an increased abundance of ^{13}C -enriched methyl carbon on the PAH.

Results and Discussion

Figure 1 shows the ^{13}C -enrichment of 1- and 2-methylnaphthalene(MN) in the carbonization products of the three FCC DO. The 1-MN isomer is consistently more enriched in ^{13}C than 2-MN in each of the oils,

indicating that the 1-position on naphthalene is more reactive toward reaction with the ^{13}C -enriched methyl radicals. This relative enrichment was previously demonstrated in the analysis of DO A by irmGCMS [7]. The greater relative reactivity of the sterically hindered α position of 1-MN with respect to the less hindered β position of 2-MN is consistent with the calculated free valence indices (FVI) of 0.452 and 0.404, respectively, where a higher FVI indicates a greater reactivity (see Fig. 2)[8]. The relative ^{13}C -enrichments of methylphenanthrene and methylpyrene isomers observed in the reaction products also correspond to predicted reactivities toward radical methylation. Among the 2,3 and 4-ring PAH analyzed in the products the highest observed enrichments are associated with methyl and dimethylpyrenes suggesting that they have the highest reactivity toward methylation reactions. The fact that these relationships are conserved in three oils of different molecular constitution attests to the presence of extensive radical methylation processes in carbonization chemistry.

The relative reactivity of dimethylnaphthalenes identified in the reaction products also respond similarly between the three oils. Figure 3 shows the enrichment for pairs of dimethylnaphthalenes in the products of DO C. In each of the three oils the grouping of 1,3/1,7- and 1,6-DMN exhibits the greatest enrichment while 2,6- and 2,7-DMN is observed to have the least enrichment. Clearly the isomers that have at least 1 methyl group in the α position show the highest enrichment.

Conclusions

Despite the fact that the three decant oils used in this carbonization study have different molecular and bulk constitution the relative reactivity of the PAH toward methylation remains consistent within each of the feedstocks. The chemical composition and constitution of the feedstock, however, greatly influences the extent of uptake of ^{13}C onto PAH.

Acknowledgments

The authors gratefully acknowledge the financial support as a grant-in-aid from the Carbide/Graphite Group, Inc.

References

1. Filley, R. M. and Eser, S., *Energy Fuels* 1997, in press.
2. Ida, T, Akada, K., Okura, T., Miyake, M., and Nomura, M., *Carbon*, 1992, **30**, 165.
3. Greinke, R.A, *Carbon*, 1990, **28**, 701.

4. Sakanishi, A., Korai, Y., Mochida, I., Yanagida, K. Noda, M., Thunori, I. and Tate, K. *Carbon*, 1992, **30**, 459.
5. Miyake, M., Ida, T., Yoshida, H., Wakisaka, S. and Nomura, M. *Carbon*, 1993, **31**, 705.
6. McKinney, D., Bortiatynski, J. and Hatcher, P., *Energy Fuels*, 1995, **9**, 578.
7. Filley, T. R., Filley, R. M. and Eser, S. and Freeman, K. H., *Energy Fuels* 1997, in press.
8. Coulson, C. A. and Streitweiser, A., *Dictionary of π -Electron Calculations*; W. H. Freeman and Co.; San Francisco, CA, 1965.

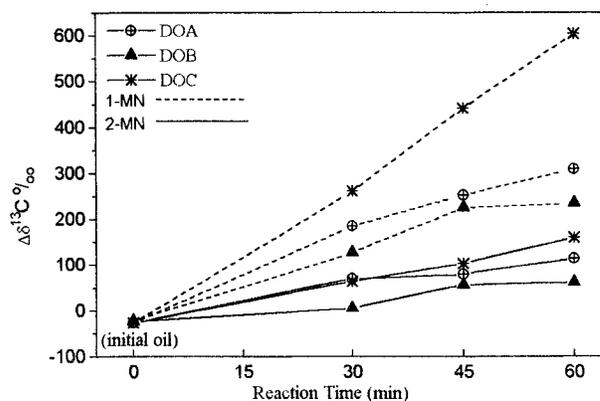


Figure 1. ^{13}C enrichment of methyl carbon on 1-, and 2-MN in DO A, DO B, and DO C reaction products.

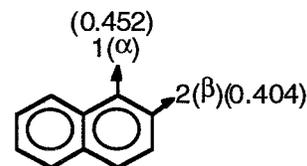


Figure 2. Free valence indices of position 1 and 2 in naphthalene.

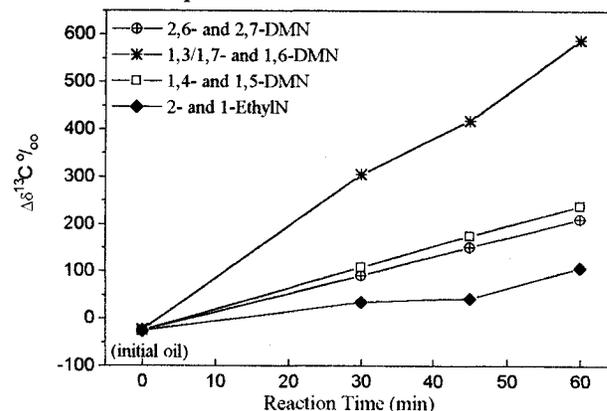


Figure 3. Average ^{13}C enrichment of methyl carbons on diMN in DO C reaction products.