

HYDROCARBON BACKBONE OF POLAR FRACTIONS

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SUMMARY

The quantity and composition of polar materials present in heavy process streams have an impact on the strategy used for their processing and the resulting yield structure. A chemical procedure was employed to deoxygenate the polar material which were later separated into aliphatic, aromatic, and residual polar fractions. These fractions were analyzed to determine their compositions. It was found that the deoxygenated hydrocarbon backbones of aliphatic and aromatic fractions derived from polar material are very similar in composition to the corresponding fractions separated from the original feed. However, structures that undergo easier oxidation are concentrated in the derived backbone fractions. The main components of the residual polar fractions obtained after deoxygenation are basic nitrogen compounds, polyheteroatom molecules, aliphatic sulfones, etc., that are resistant towards chemical processing.

INTRODUCTION

Most of the results published in the open literature concentrate on the analysis of polar compounds with a single functional group. For example, the carboxylic acids have been widely investigated (1-4). Seifert identified carboxylic acids associated with a variety of aliphatic, aromatic and heterocyclic (S- and N-containing) backbones (1,2). Cason isolated and identified isoprenoidal acids from California crudes (3,4). Sulfoxides represent another large group of polar compounds particularly in crudes that have a high total sulfur content. Strausz et al. described a method for converting polar sulfoxide molecules to low polarity sulfides that can later be separated from the polar matrix by chromatographic techniques (5). Basic nitrogen compounds represent the majority of nitrogen in the polar fraction (6-11). However, neutral and acidic nitrogen compounds with polar functional groups (e.g. carbonyl) are also present in the polar fraction (1). In this work we attempted to analyze the polar fraction of a crude and account for all polar functionalities and the hydrocarbon backbone with which these polar functionalities are associated.

EXPERIMENTAL PART

Reagents.

All solvents used were reagent or HPLC grade. Silica gel, mesh 100-200, Grade 923, supplied by Davison Chemical, was activated in an oven at 500°F for 24 hours. Alumina was purchased from ICN Biochemicals.

Instruments.

The GC/MS chromatograms were collected on Finnigan TSQ-70 and Kratos MS 80 instruments. The gas chromatographs on both instruments were equipped with J&W Scientific DB-5 columns, 30 m, 0.25 mm ID, 0.25 μ m film thickness. Kratos MS 80 instrument was used to acquire field ionization mass spectra.

Simultaneous chromatograms (GC/FID, GC/FPD-sulfur) were recorded on a Varian 3400 instrument, using a J&W DB-5 column, 30 m, 0.53 mm ID, 1.5 μ m film thickness.

The FTIR spectra were recorded on a Mattson Sirius 100 instrument.

PROCEDURE DESCRIPTION.

The polar fraction, 2.5 weight percent of the original material, was separated from the 550°F-1050°F fraction of a crude on silica gel. A sequence of hexane and toluene were used to elute aliphatic and aromatic fractions. The polar fraction was eluted with 50/50 vol% methanol/toluene and 50/50 vol% methylene chloride/acetone. The chemical procedure used to deoxygenate the polar fraction is similar to that described by Seifert et. al. (2). The sequence of LAH reduction, tosylation, and LAH reduction on the polar fraction gave an overall yield of 90.1 weight percent. Mass loss is expected due to removal of functional groups; however, some loss may be due to sample handling.

The chemically processed material was separated on silica gel into an aliphatic (Aliphatic Backbone), an aromatic (Aromatic Backbone), and a residual polar (Polar Backbone) fractions. The Aliphatic Backbone fraction was eluted with hexane, the Aromatic Backbone fraction was eluted with toluene, and the Polar Backbone fraction was eluted with 50/50 vol% methanol/toluene and 50/50 vol% methylene chloride/acetone. The aromatic fraction derived from the chemically processed polar fraction was further separated on alumina impregnated with 4% of silver nitrate (12). Aromatic Backbone Fraction-1 (ABF-1) and Aromatic Backbone Fraction-2 (ABF-2) were eluted with toluene, Aromatic Backbone Fraction-3 (ABF-3) with 5/95 vol% methanol/toluene, and Backbone Fraction-4 (ABF-4) with 30/70 vol% methanol/toluene and 50/50 vol% methanol/toluene. Residual silver nitrate was removed from ABF-3 and ABF-4 by extraction with distilled water.

RESULTS AND DISCUSSION

Selective reactions, outlined in the Experimental Part, remove reactive functional groups responsible for the polarity of molecules present in the polar fraction. Lithium aluminum hydride (LAH) reduces functional groups such as carboxylic acids, aldehydes, esters, ketones, acid anhydrides, and amides to hydroxyl groups (13). Then, hydroxyl groups are converted to the corresponding tosylates, which are later reduced with LAH to the hydrocarbon backbone (2).

The polar functional group can be associated with an aliphatic or an aromatic structure or attached to an aliphatic fragment of the aromatic molecule (naphthenic ring or alkyl side chain of an aromatic molecule). Also, a polar functional group can be attached to structures bearing a heteroatom.

Sulfoxides, another large group of polar compounds, are reduced to sulfides during the first reduction with LAH (5). Sulfides remain intact during tosylation and the second reduction with LAH.

Sulfones of thiophenes are easily reduced with LAH; however, sulfones of sulfides are difficult to convert back to sulfides. Reduction reactions of various functional groups with LAH are summarized by Hudlicky (13).

Infra-red

Infrared spectroscopy was used to quantify the contribution of various functional groups using average absorption coefficients reported in the literature (14,15). The result of this quantitative analysis is as follows: carboxylic acids and other carbonyls 8 weight percent; sulfoxides 47 weight percent; phenols and alcohols 12 weight percent.

Separations

The Aliphatic Backbone fraction represents only 4.5 weight percent of the chemically

processed material (Table 1). Table 2 shows the group type distribution of the Aliphatic Backbone fraction and of the aliphatic fraction separated from the original crude fraction by a similar method. The Aliphatic Backbone derived from the polar fraction has a strong paraffinic character and absence of sulfur compounds (Figure 1). It is apparent from these data that the character of both aliphatic materials is similar.

The chemically processed polar fraction contains 65.2 weight percent as the Aromatic Backbone fraction (Table 1). This material contained high concentration of sulfides (Figure 1). This group of compounds was further separated from the rest of the aromatic matrix, as outlined in the Experimental Part.

The first two fractions eluted with toluene, were relatively small. The weight percent distributions and elemental analyses for ABF-1 and ABF-2 are shown in Table 1. ABF-1 and ABF-2 consist of aromatic hydrocarbons, thiophenic compounds, and nitrogen compounds having a pyrrolic ring that originated from the polar precursors. Pyrrolic nitrogen compounds are significant contributors to ABF-1 and ABF-2. Calculated from the average molecular weight and nitrogen content, determined by field ionization mass spectrometry (FIMS), ABF-1 and ABF-2 contain 43 and 63 weight percent of pyrrolic compounds, respectively. Mononaphthenocarbazole is the most abundant in this series.

Thiophenic compounds were identified in ABF-1 and ABF-2. Thiophenes could have originated from the corresponding sulfones or from thiophenes that had functional groups (R) reducible with LAH to hydroxyl. Based on sulfur measurements and average molecular weight from FIMS, ABF-1 and ABF-2 contain 6 and 11 weight percent of thiophenes, respectively.

ABF-3 and ABF-4 derived from the polar fraction constitute a majority of the total Aromatic Backbone fraction (Table 1). These two fractions contain predominantly sulfides and a small amount of pyrroles. Sulfides present in the ABF-3 and ABF-4 are very similar to the sulfides found in the corresponding fractions separated, by similar method, from the original crude fraction. Based on molecular weight from FIMS and nitrogen content, ABF-3 and ABF-4 contain 16 and 5 weight percent of pyrrolic nitrogen, respectively.

It is remarkable that the chemically processed polar fraction contains 46.6 weight percent of material defined as sulfides. This high concentration of sulfides is in very good agreement with 47 weight percent of sulfoxides quantified by IR. Pyrroles, aromatic hydrocarbons, and thiophenic compounds represent 12.9, 0.9, and 4.8 weight percent of the total polar fraction, respectively.

The residual polar material, Polar Backbone, represents 29.3 weight percent of the chemically processed polar fraction and contains 3.26 weight percent sulfur and 2.57 weight percent nitrogen (Table 1 and Figure 1). The Polar Backbone has substantial aromatic character (32% aromatic C and 9% aromatic H). Sulfur present in this fraction may exist in structures with polyheteroatoms, or sulfones and sulfoxides that are resistant towards reduction with LAH. Nitrogen is present mainly in the form of basic nitrogen compounds or polyheteroatom structures (8-13). Limited information was obtained from these data due to the high complexity of this fraction. More research is needed to characterize basic nitrogen and polyheteroatom compounds.

CONCLUSIONS

Removal of oxygen-bearing functional groups from the polar fraction produced non-aromatic and aromatic hydrocarbons (including those containing heteroatoms), and sulfides.

The low level of Aliphatic Backbone in the polar fraction results from minimal

biodegradation of the original crude. Sulfoxides represent almost half of the polar fraction. It is suspected that sulfoxides may result from the oxidation during sample handling; however, indigenous sulfoxides can not be excluded. Pyrrolic nitrogen molecules that bear a polar group represent a significant part of the polar fraction. Pyrrolic molecules that contain naphthenic ring(s) are concentrated in the polar fraction.

Polar fraction bear a striking resemblance to non-polar material of the original crude. That is, polar fraction differ in functionality, but its backbone is consistent with compounds from the non-polar material. We believe that this observation can be applied to the polar materials from other petroleum feeds and products.

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TABLE 1. MASS, SULFUR, AND NITROGEN BALANCES FOR CHEMICALLY PROCESSED POLAR FRACTION.

	Mass Wt %	Sulfur in Sample wt% (*)	Sulfur in Total Polars wt%	Nitrogen in Sample wt% (**)	Nitrogen in Total Polars wt%
Starting Material (***)	100	3.97	3.97	1.28	1.28
Aliphatic Backbone	4.5	0.00	0.00	0.00	0.00
Aromatic Backbone	65.2	NM	3.09	NM	0.69
Total			(****)		
Aromatic Backbone Fraction 1 (ABF-1)	7.6	0.59	0.05	1.96	0.15
Aromatic Backbone Fraction 2 (ABF-2)	3.8	1.03	0.07	2.99	0.11
Aromatic Backbone Fraction 3 (ABF-3)	39.3	4.96	1.95	0.99	0.39
Aromatic Backbone Fraction 4 (ABF-4)	14.5	7.04	1.02	0.32	0.04
Polar Backbone	29.3	3.26	0.95	2.57	0.75
Balance	99.0		4.04		1.44

(*) Measured by D 1552
 (**) Estimated from FIMS

(***) Charge to LC column after reactions
 (****) Sum of ABF-1, ABF-2, ABF-3, and ABF-4

TABLE 2. GROUP TYPE DISTRIBUTION IN ALIPHATIC BACKBONE FRACTION AND ALIPHATIC FRACTION SEPARATED FROM ORIGINAL MATERIAL.

Compounds	Aliphatic Backbones	Aliphatics-original material
Paraffins	46.5	50.5
Mononaphthenes	17.4	15.1
Dinaphthenes	11.3	13.0
Trinaphthenes	6.6	7.6
Tetranaphthenes	7.9	6.3
Pentanaphthenes	7.8	5.0
Hexanaphthenes	0.0	1.7

FIGURE 1. GC TRACES (FID & FPD-SULFUR) FOR CHEMICALLY PROCESSED POLAR FRACTION. (A) ALIPHATIC BACKBONE, (B) AROMATIC BACKBONE, (C) POLAR BACKBONE

