SELECTIVE SEPARATION AND IDENTIFICATION OF OLEFINS
IN PETROLEUM AND SYNTHETIC FUEL NAPHTHA

MARC A. POIRIER AND ALBERT E. GEORGE

FEBRUARY 1981

SELECTIVE SEPARATION AND IDENTIFICATION OF OLEFINS
IN PETROLEUM AND SYNTHETIC FUEL NAPHTHA

by

Marc A. Poirier* and Albert E. George**

ABSTRACT

An effective analytical procedure for the selective separation and identification of olefins in petroleum and synthetic fuel naphtha is described. The method is based on the specific and quantitative conversion of olefins to alcohols by the hydroboration-oxidation reaction. The latter selectively converts olefins to alcohols which are subsequently separated from the hydrocarbon mixture by chromatography on alumina. Conversion of the olefins to alcohols was monitored by proton magnetic resonance (PMR).

A gas chromatograph interfaced with a quadrupole mass spectrometer (GC-MS) was used to identify the individual alcohols, using retention indices of pure compounds as well as library search data. Structural assignment to the parent olefins is based on the stereochemistry of the hydroboration reaction.

The procedure was applied to two synthetic fuel naphthas produced by thermal and catalytic processing of the Lloydminster heavy oil. Results indicate that the olefins are produced during processing. The olefins of the catalytic naphtha are of predominantly higher average molecular weight (C_7-C_{10}) than the thermal naphtha (C_5-C_8). Chemical configurations have been assigned for twenty-four different olefins in both products.

*Research Scientist and **Acting Section Head, Research on Bituminous Substances Section, Synthetic Fuels Research Laboratory, Energy Research Laboratories, CANMET (Canada Centre for Mineral and Energy Technology), Energy, Mines and Resources Canada, Ottawa, Canada

INTRODUCTION

The application of heat to bitumens, crude and heavy oils in the course of refining and processing frequently produces olefins. Chemical characterization of the olefinic components in the naphtha of the processing products is necessary to understand the mechanism and effect of the catalyst and changing reactor conditions on the formation of these components.

A method for the determination of olefinic content, based on hydroboration-oxidation reaction of the olefins, resulting in quantitative conversion to alcohols has been developed in our laboratory[1]. In that method, the alcohol mixture was recovered from the hydrocarbon fraction by elution on an alumina column.

This reaction procedure coupled with GC-MS has been used in this work to establish a highly selective analytical approach for the identification of olefins in petroleum and synthetic fuel naphthas.

Several workers have used GC-MS technique for the separation and characterization of hydrocarbons in the gasoline range[2-4]. But without this selective separation of olefins in the form of alcohols, characterization by GC-MS would be difficult because of the overlap of olefins with paraffins in the gas chromatographic separation, as well as the similarity of mass spectral parent ions of linear olefins with those of cycloalkanes having equivalent carbon numbers. Hydrocarbon-type separation of olefins, saturates and aromatic compounds by high performance liquid chromatography (HPLC) has been investigated by some workers[5,6]. No structural elucidation of olefins was made to show the selectivity of the methods.

We applied our analytical approach to two synthetic fuel naphthas produced from processing the Lloydminster heavy oil. Identification of alcohols was accomplished by correlations with retention indices and boiling points of pure alcohols as well as mass spectral library search data. Structural assignment to the parent olefins is based on stereochemistry of the hydroboration reaction, which proceeds to an anti-Markovnikov addition of diborane to the olefinic double bond[7]. Twenty-four different olefinic components have been identified in two naphthas resulting from both thermal and catalytic processing of the heavy oil.

A schematic diagram of the separation and identification procedure is shown in Fig. 1.

EXPERIMENTAL

Samples

1. Naphtha (i.b.p.-200°C) obtained by distillation of virgin Lloydminster oil.

2. Naphtha (i.b.p.-200°C) obtained by distillation of thermally processed Lloydminster oil.

3. Naphtha (i.b.p.-200°C) obtained by distillation of catalytically processed Lloydminster oil.

4. Synthetic alcohol mixture prepared by dissolving 0.1 mL of each individual alcohol in 2 mL pentane (Table 1).

Hydroboration Procedure

About 2.2 g of petroleum distillate naphtha is introduced to a 250 ml three-neck round bottom flask containing 25 mL of dry ether equipped with a magnetic stirring bar, a condenser and a dropping funnel. The system is purged with nitrogen, and a large excess (1 mL) of borane-methyl sulphide complex (10M in BH_3) is added with a syringe slowly to the flask at 0°C through a septum[1]. The solution is agitated at room temperature for 1.5 h; the reaction mixture is then cooled to 0°C and 15 mL of 3N sodium hydroxide is added slowly, followed by 15 mL of 30% hydrogen peroxide solution. The solution is transferred to a 250 mL separating funnel, diluted with 100 mL of ether and washed (4 x 100 mL) with saturated NaCl solution and with 100 mL water. The resulting ether phase is dried over anhydrous sodium carbonate, filtered and solvent removed on rotary evaporator under slight vacuum.

The resulting product is percolated on a 10 g alumina glass column (30 cm x 2 cm O.D.) with 60 mL of 1% benzene in pentane eluent to separate the hydrocarbon portion from the alcohols. The latter are recovered from the column by elution with 125 mL dichloromethane and the solvent removed as above. The procedure is illustrated in Fig. 1.

Determination of the Olefinic Content

The olefinic content was determined according to the hydroboration-oxidation procedure that has been developed in our laboratory[1].
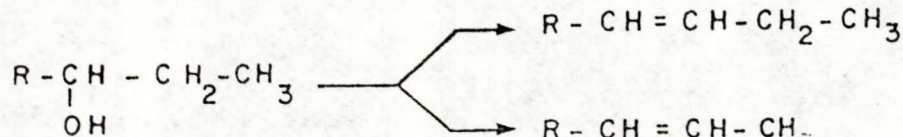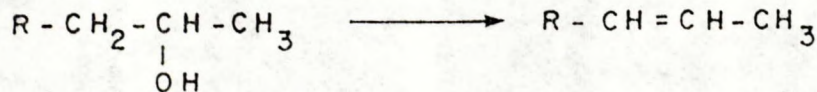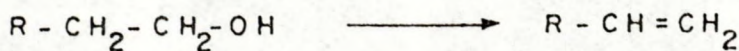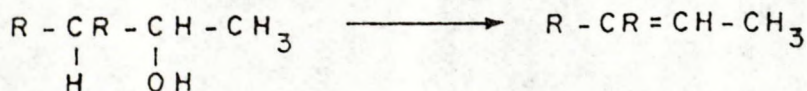
Sample Analysis

Twenty-two individual linear, branched and cyclic alcohols (Table 1) were chromatographed together with a series of n-alkanes on a 4m x 3 mm O.D. packed column coated with 3% OV-25 on chromosorb W (AW, DMCS, 100-120 mesh size).

Mass spectral analyses were performed using a Finnigan 4000 gas chromatograph-quadrupole spectrometer equipped with a precisely controlled oven temperature, programmed from 60 to $200^{\circ}C$ at $4^{\circ}/min$ and interfaced with a Incos Nova 3 computer. Carrier gas flow rate was 20 mL/min. Two alcohol mixtures resulting from hydroboration of the two naphtha products were analyzed by GC-MS.

The PMR spectra were obtained on a Varian CFT-20 spectrometer. The spectra were recorded in deuterated chloroform ($CDCl_3$).

RESULTS AND DISCUSSION

Hydroboration reaction being controlled by stereoelectronic effects converts olefins to the less substituted carbinols, e.g., tertiary alcohols having no alkyl groups on the adjacent carbon and postulated by the mass spectra library computer should be excluded. According to the stereochemistry of hydroboration the 1-alkanol is derived from 1-alkene and the 2-alkanol from 2-alkene. In the case of the 3-alkanol, this alcohol can be formed from either the 2-alkene or the 3-alkene because addition of diborane to give 3-alkanol can be formed from one or the other. This can be illustrated by the following equations:

$$R - \underset{\underset{H}{|}}{C}R - \underset{\underset{OH}{|}}{C}H - CH_3 \longrightarrow R - CR = CH - CH_3$$

$$R - CH_2 - CH_2 - OH \longrightarrow R - CH = CH_2$$

$$R - CH_2 - \underset{\underset{OH}{|}}{C}H - CH_3 \longrightarrow R - CH = CH - CH_3$$

$$R - \underset{\underset{OH}{|}}{C}H - CH_2 - CH_3 \longrightarrow \begin{cases} R - CH = CH - CH_2 - CH_3 \\ R - CH = CH - CH_3 \end{cases}$$

R = long chain alkyl group

Structural assignment to the identified olefins in both naphthas has been made on the basis of the separated alcohols (Table 2), according to the preceding interpretation.

Retention indices and boiling points of 22 pure alcohols, chromatographed under the previously described conditions, are listed in Table 1. The boiling points of these alcohols and their corresponding parent olefins adequately covers the naphtha boiling range (i.b.p.-200°C). Retention indices of the pure alcohols show linear boiling point distribution on the OV-25 column (Fig. 2). This figure was used in identifying the alcohols from synthetic fuel naphtha.

Lloydminster Synthetic Naphtha

Olefinic content of the virgin naphtha is very low, relative to the other two synthetic naphthas, Table 3. This suggests that the olefins are generated during processing. Olefins in the naphtha product from thermal processing are 27% higher than that of the catalytic product. The chromatographic data indicate that the olefins of the latter are of predominantly higher average molecular weight (C_7-C_{10}) than those of the thermally processed (C_5-C_8) naphtha. Considering that processing conditions are similar in both cases, these results are explained by the relatively restricted cracking to smaller molecules in the presence of the catalyst.

A typical chromatogram (Fig. 3) shows the separation of alcohols in the naphtha resulting from thermal processing. No aromatic protons have been detected by PMR in eigher of the two alcohol mixtures from both naphthas, which indicates the absence of aromatic olefins. The identified alcohols and corresponding parent olefins for both synthetic naphthas are shown in Table 2.

This approach to the analysis of olefins in complex hydrocarbon mixtures has several advantages. The separation is not only selective for olefins in the form of alcohols but also provides considerably larger amounts of alcohols than could be separated by preparative HPLC. The separation of olefins from a hydrocarbon mixture sample would make further separations of the saturates and aromatics by chromatographic methods considerably more feasible.

This analytical approach could also be extended to the olefins in higher boiling range fractions of petroleum and synthetic fuels, where separation is usually more complicated. We are currently conducting research work in this area.

CONCLUSION

The hydroboration-oxidation procedure permits highly selective separation of olefins in the form of alcohols. It provides a pure alcohol mixture for identification by GC-MS, and thus offers new possibilities in the analysis of olefins in petroleum and synthetic fuels naphthas. The position of the olefinic double bond can be established by correlation to the stereochemistry of the hydrocarbon reaction.

REFERENCES

Fuel, 60, 194, 1981.

1. Poirier, M.A. and George, A.E. (~~accepted for publication in Fuel~~).

2. George, A.E., Smiley, G.T. and Sawatzky, H. "Rapid chromatographic procedure for characterizing hydrocarbons in synthetic fuel naphtha", CANMET Report 79-17, March 1979.

3. Merchant, P. Jr. Anal. Chem, 40, 2153, 1968.

4. Sanders, W.N. and Maynard, J.B. Anal. Chem, 40, 527, 1968.

5. McKay, J.F. and Lathan, D.R. Anal. Chem, 52, 1618, 1980.

6. Suatoni, J.C. and Swab, R.E. J. Chrom. Sci., 18, 375, 1980.

7. Pasto, D.J. and Klein, F.M. J. Org. Chem 33, 1468, 1968.

Table 1 - Retention index (R.I.) and boiling
point of reference alcohols

Alcohols	B.P. (^{O}C)	R.I.
3-pentanol	117	806
2-pentanol	118	826
3,3-dimethyl-2-butanol	120	832
2-methyl-1-butanol	130	836
3-methyl-1-butanol	130	836
4-methyl-2-pentanol	132	862
2-methyl-3-pentanol	128	866
3-hexanol	135	902
2,4-dimethyl-3-pentanol	140	906
1-pentanol	137	909
2-hexanol	136	910
2-ethyl-1-butanol	146	948
2-methyl-1-pentanol	148	948
1-hexanol	157	1005
2-heptanol	161	1008
cyclohexanol	160	1045
1-heptanol	176	1104
2-octanol	175	1107
1-octanol	196	1218
1-nonanol	215	1308
1-decanol	231	1408
1-undecanol	255	1508

Table 2 - Alcohols Identified in the Naphtha of Processed Lloydminster Oil

Alcohol	B.P., °C	Retention Index	Corresponding Parent Olefin
2-pentanol	118	826	2-pentene*
3-methyl-2-butanol	112	775	2-methyl-2-butene*
2,3-dimethyl-2-butanol	120	832	2,3-dimethyl-2-butene
4-methyl-2-pentanol	132	862	4-methyl-2-pentene
2-methyl-3-pentanol	128	866	2-methyl-2-pentene
3-hexanol	135	902	2-hexene or 3-hexene
2-hexanol	136	910	2-hexene
2-ethyl-1-butanol	146	948	2-ethyl-1-butene
2-methyl-1-pentanol	148	948	2-methyl-1-pentene
2-methylcyclopentanol	155	999	1-methylcyclopentene
1-hexanol	157	1005	1-hexene
2-heptanol	161	1008	2-heptene*
cyclohexanol	160	1045	cyclohexene
3-heptanol	160	1045	3-heptene or 2-heptene*
2-methylcyclohexanol	164	1046	1-methylcyclohexene
2-octanol	175	1107	2-octene*
1-heptanol	176	1104	1-heptene
3-octanol	179	1124	3-octene or 2-octene*
2-ethyl-1-hexanol	184	1150	2-ethyl-1-hexene*
1-octanol	196	1218	1-octene*
1-nonanol	215	1308	1-nonene*
1-decanol	231	1408	1-decene*
1-undecanol	255	1508	1-undecene*
1-dodecanol	261	1550	1-dodecene*

* These olefins are present in both the thermal and catalytic naphthas.
  Other olefins are only present in the thermal product.

Table 3 - Olefinic content of Lloydminster naphthas
(determined by hydroboration-oxidation
procedure)

Naphtha	wt % Olefins
Naphtha from distillation of virgin oil	0.5
Naphtha from thermally processed oil	26.8
Naphtha from catalytically processed oil	19.5

CAPTIONS

Figure 1:   Separation and Identification scheme

Figure 2:   Retention data of the n-alcohols on a OV-25 column

Figure 3:   Chromatogram of alcohols separated from the thermal naphtha

Figure 1

```
                    ┌─────────────────────┐
                    │     N A P H T H A    │
                    │   ìьр  -  2 0 0 °C   │
                    └─────────────────────┘
                                │
                    HYDROBORATION - OXIDATION
                                │
          ┌─────────────────────────────────────────────┐
          │   SATURATES,  AROMATICS  AND  ALCOHOLS       │
          └─────────────────────────────────────────────┘
                                │
                    ALUMINA CHROMATOGRAPHY
                                │
          ┌─────────────────────────────────────────────┐
          │                                             │
   PENTANE-BENZENE                            DICHLOROMETHANE
          │                                             │
┌──────────────────────┐                  ┌──────────────────────┐
│ SATURATES, AROMATICS  │                  │     A L C O H O L S  │
└──────────────────────┘                  └──────────────────────┘
                                                       │
                                           GAS CHROMATOGRAPHY
                                           (3% OV-25 COLUMN )
                                                       │
                                           RETENTION INDICES
                                           COMPOUND IDENTIFICATION
                                           (QUADRUPOLE M.S., COMPUTER )
```

ALCOHOLS

RETENTION INDICES (X 100)