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IDENTIFICATION OF HYDROCARBON
TYPES IN "ULTRASENE"

by

R. N. Wilhite

Analytical Chemistry Division

April 1961

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IDENTIFICATION OF HYDROCARBON TYPES IN "ULTRASENE"

by

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April 1961

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ABSTRACT

The C₁₁ - C₁₄ components of a sample of "Ultrasene" were identified as normal- and iso-paraffins; mono-, bi-, and tri-cycloparaffins; alkylbenzenes; indans; indenes; naphthalenes; and acenaphthenes. The aromatic content of this sample was 3.0 vol %.

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IDENTIFICATION OF HYDROCARBON TYPES IN "ULTRASENE"

INTRODUCTION

In the Purex process, radiolytic and chemical degradation of the organic solvent* produce compounds that complex fission products, particularly zirconium, and retain them in the organic stream. Caustic washing of the organic solvent before reuse does not substantially reduce the high radiation level of the solvent or improve the separation of fission product activity from the uranium and plutonium during the next extraction cycle⁽¹⁾. Studies of the chemical and radiolytic degradation of pure hydrocarbons have shown that certain types of hydrocarbons are more easily degraded than are others to form these zirconium ligands.⁽²⁾ Olefins and specific aromatic types were shown to be precursors of zirconium ligands.

This report describes the application of low ionizing voltage mass spectrometry to the identification of hydrocarbon types in "Ultrasene". Knowledge of the composition of "Ultrasene", the refined kerosene diluent, will assist in the identification of the precursors of zirconium ligands.

SUMMARY

Nine hydrocarbon types corresponding to the formula C_nH_{2n+z} , where z is any even integer between -14 and +2, were identified in the C_{11} , C_{12} , C_{13} , and C_{14} components of an aromatic concentrate from a sample of "Ultrasene". Identifications of the hydrocarbon types were made on the bases of low ionizing voltage mass spectra and of retention characteristics on a silica gel chromatographic column. Infrared and ultraviolet absorption spectrophotometry and gas-liquid chromatography were employed to verify the classes of compounds as normal- and iso-paraffins; mono-, bi-, and tri-cycloparaffins; alkylbenzenes; indans; indenenes; naphthalenes; and acenaphthenes. The composition of the aromatic hydrocarbons was estimated from the data. The total aromatic content of the sample was 3.0 vol %.

DISCUSSION

THEORETICAL BACKGROUND

The identification of hydrocarbon type by mass spectrometry is made by determining the molecular mass of the hydrocarbon from the mass spectrum and fitting the mass to the general formula C_nH_{2n+z} where n (carbon number) is the number of carbon atoms in the molecule and z

* 30 vol % tri-n-butyl phosphate, 70 vol % "Ultrasene", a refined kerosene product of the Atlantic Refining Co.

(hydrocarbon type) is an even integer between +2 and 2-2n. Compounds of same hydrocarbon type but different carbon number differ in mass by multiples of fourteen atomic mass units (a.m.u.), the CH₂ unit. Two compounds of the same mass can exist as separate hydrocarbon types in adjacent carbon number groups as shown in Table I.

Table I

Molecular Weights of Hydrocarbons
of General Formula $C_n H_{2n+z}$

Hydrocarbon Type, z	Carbon Number, n			
	11	12	13	14
-16	138	152	166	180
-14	140	154	168	182
-12	142	156	170	184
-10	144	158	172	186
- 8	146	160	174	188
- 6	148	162	176	190
- 4	150	164	178	192
- 2	152	166	180	194
0	154	168	182	196
+ 2	156	170	184	198

The molecular masses of many hydrocarbons in "Ultrasene" are obscured by the spectra of hydrocarbons of higher mass, and, since the determination of hydrocarbon type is dependent on identification of molecular mass, special techniques are required to eliminate or minimize these interferences. Mass spectra, obtained for most C₁₀ - C₁₄ hydrocarbons by means of 50-70 volt ionizing electrons, consist of small molecular mass peaks (parent peaks), small isotope and fragment peaks in the parent peak region, large fragment peaks in the C₂ - C₆ region, and large peaks from stable ring structures within the molecule.⁽³⁾ Some fragment peaks of the hydrocarbons of high mass may be superimposed upon the parent peaks of hydrocarbons of lower mass so that the presence of the latter may be unsuspected.

Hydrocarbon types are more easily identified if the mass spectra are simplified by the use of low ionizing voltage techniques. Molecular ions are the principal products of the ionization of hydrocarbons by electrons with energies in the range of 8-12 electron volts^(4,5). The resulting mass spectra are known as low ionizing voltage mass spectra (LIVMS), and consist of large parent peaks and a few small

fragment and isotope peaks. Although the number and size of fragment peaks increases rapidly with increased branching in the hydrocarbon molecule, the spectra obtained by low ionizing voltage allow adequate discernment of molecular mass peaks for a petroleum product such as "Ultrasene".

A preliminary separation of "Ultrasene" into two fractions containing hydrocarbon types +2 through -10 and -12 through -24 is necessary to eliminate the presence of two indistinguishable hydrocarbon types at a single molecular mass, e.g., $C_{12}H_{22}$ and $C_{13}H_{10}$. In practical applications, hydrocarbons are more easily separated into fractions of non-aromatic, mono-nuclear aromatic, and polynuclear aromatic content. The separation of non-aromatic (hydrocarbon types +2 through -4) and aromatic (hydrocarbon types -6 through -14) fractions was adequate for "Ultrasene".

EQUIPMENT

LIVMS were obtained on a modified Consolidated Electrodynamics Corporation model 21-103 mass spectrometer. The source control of the mass spectrometer was modified as described by Lumpkin⁽⁶⁾ to permit use of low voltages in the repeller and ionizing voltage circuits. A model 36 Vibrating Reed Amplifier (Applied Physics Corporation) was installed to increase the sensitivity of the mass spectrometer. The resolving slit of the analyzer tube was narrowed from 0.030 to 0.012 inch to provide resolution of adjacent mass units at 200 a.m.u.

The sample inlet system was maintained at 150°C to vaporize the samples, which were introduced by means of a capillary dipper and heated gallium-sealed frit. When the inlet system was operated at temperatures much below 150°C the "pumpout" time for removal of spent sample was excessively long and "memory" for the preceding sample was a problem. At 150°C, a "pumpout" time of 30 minutes was required to avoid "memory" difficulties.

EXPERIMENTAL PROCEDURE

A separation of hydrocarbon types in a sample of "Ultrasene" into paraffinic and aromatic fractions was made by liquid-solid chromatography with a silica gel column after the fashion of Rossini, et al⁽⁷⁾.

The "Ultrasene" that was studied* contained 3.0 vol % aromatic material according to an analysis by the ASTM procedure, D1319-56T. In order to separate and recover enough aromatic material to examine, 500 ml of "Ultrasene" was sorbed onto a silica gel column, and was eluted with isopropyl alcohol. The final 25-ml portion of the hydrocarbon was collected separately. In order to obtain a better

* Purchased in a tank car lot from Atlantic Refining Co. in February 1960.

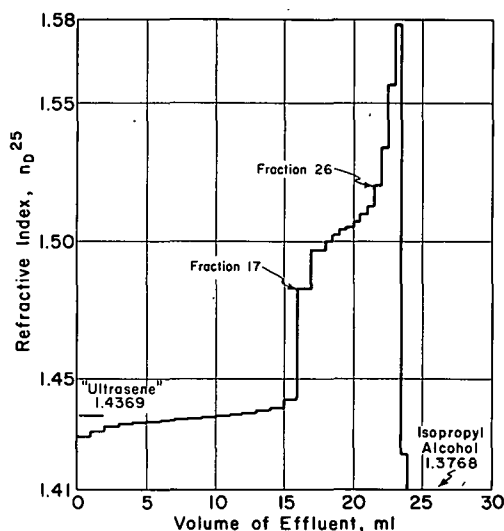


FIG. 1 REFRACTIVE INDICES OF CHROMATOGRAPHIC FRACTIONS OF AROMATIC CONCENTRATE

separation of the paraffinic and aromatic materials, the 25-ml portion of aromatic concentrate was rerun on a fresh silica gel column and 30 small fractions were collected in the elution step. The refractive indices, given in Figure 1, of the earlier fractions of the aromatic concentrate are lower than or equal to that of the "Ultrasene", while at fraction 17 and at fraction 26 there are sudden increases in the refractive index. These increases in refractive index are due to elution of the mono- and di-nuclear aromatic portions, respectively. Fractions 1-18 were 1.0 ml each and fractions 19-30 were 0.5 ml each. Approximately 7 ml of aromatic material was obtained.

LIVMS were obtained for these fractions over the range of 100-206 a.m.u. The ionizing current of the mass spectrometer was 20 microamps, the ionizing voltage was 8.6 volts, and the repellers were held at +2.6 volts. Because of interaction of the low potentials of the repellers and the filament, the true ionizing voltage was not known, but its actual value was not critical in this work.

RESULTS

The mass spectral peaks for each fraction were identified by mass, and the peak heights were compared with the elution time from the silica gel column. The comparison of peak heights for mass 170 with the chromatographic fraction is shown in Figure 2.

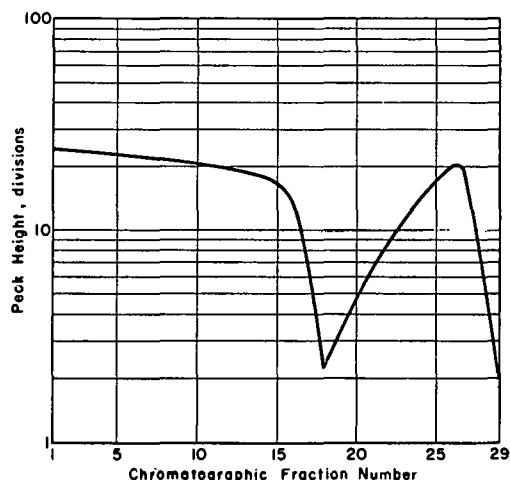


FIG. 2 ELUTION CURVE FOR COMPOUNDS OF MASS 170

The discontinuity of the curve at about fraction 18 indicates a break between two hydrocarbon types. These types correspond to $C_{12}H_{26}$, a paraffin, and $C_{13}H_{14}$, a substituted naphthalene. Nine hydrocarbon types were identified from similar plots of molecular mass peaks in the C_{11} , C_{12} , C_{13} , and C_{14} groups of the "Ultrasene".

The elution curves for the hydrocarbon types identified in the C_{12} group (Figure 4) are typical of those for the other carbon number groups shown in Figures 3, 5, and 6. Four paraffin and cycloparaffin types (z equal to +2, 0, -2, and -4) were eluted in the first sixteen fractions and five aromatic types (z equal -6, -8, -10, -12, and -14) were eluted in the final thirteen fractions. Type -14 was concentrated in the last two fractions.

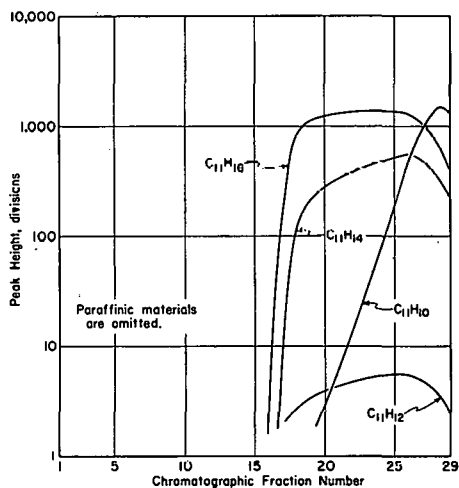


FIG. 3 ELUTION CURVES OF C_{11} HYDROCARBON TYPES

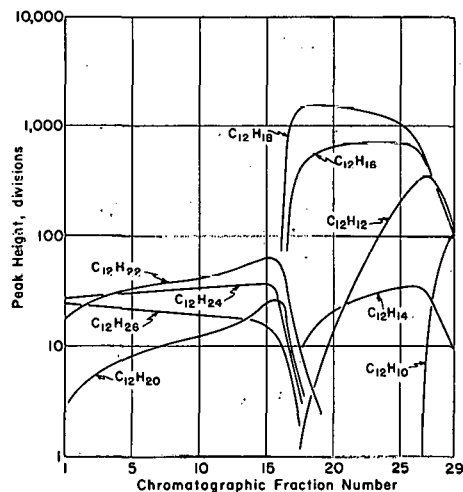


FIG. 4 ELUTION CURVES OF C_{12} HYDROCARBON TYPES

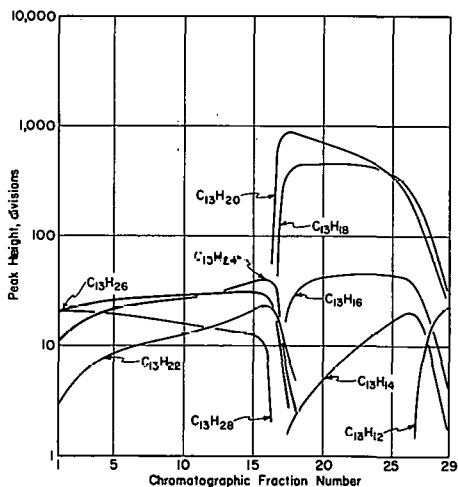


FIG. 5 ELUTION CURVES OF C_{13} HYDROCARBON TYPES

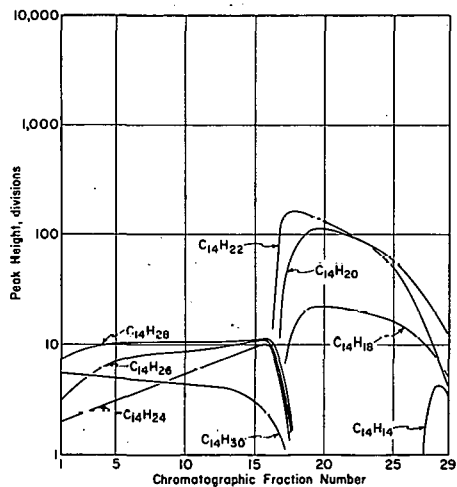


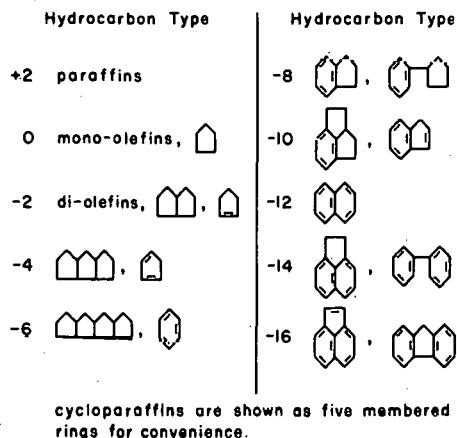
FIG. 6 ELUTION CURVES OF C_{14} HYDROCARBON TYPES

The hydrocarbon types found in each carbon number group ($C_{11} - C_{14}$) are summarized in Table II. No type -16 was found. Type -14 was found only in the C_{12} , C_{13} , and C_{14} groups. Type -12 was found in all but the C_{14} group. Types -10 through +2 were in all four groups.

Table II
Hydrocarbon Types Found in the $C_{11} - C_{14}$
Groups of "Ultrasene"

Hydrocarbon Type, z	Carbon Number, n			
	11	12	13	14
-16	(a)	(a)	(a)	(a)
-14	(a)	$C_{12}H_{10}$	$C_{13}H_{12}$	$C_{14}H_{14}$
-12	$C_{11}H_{10}$	$C_{12}H_{12}$	$C_{13}H_{14}$	(a)
-10	$C_{11}H_{12}$	$C_{12}H_{14}$	$C_{13}H_{16}$	$C_{14}H_{18}$
- 8	$C_{11}H_{14}$	$C_{12}H_{16}$	$C_{13}H_{18}$	$C_{14}H_{20}$
- 6	$C_{11}H_{16}$	$C_{12}H_{18}$	$C_{13}H_{20}$	$C_{14}H_{22}$
- 4	$C_{11}H_{18}$	$C_{12}H_{20}$	$C_{13}H_{22}$	$C_{14}H_{24}$
- 2	$C_{11}H_{20}$	$C_{12}H_{22}$	$C_{13}H_{24}$	$C_{14}H_{26}$
0	$C_{11}H_{22}$	$C_{12}H_{24}$	$C_{13}H_{26}$	$C_{14}H_{28}$
+ 2	$C_{11}H_{24}$	$C_{12}H_{26}$	$C_{13}H_{28}$	$C_{14}H_{30}$

(a) Not Detected



Identification of specific classes of compounds by mass spectrometric means alone was complicated by the plurality of classes within a single hydrocarbon type, i.e. mono-olefins and mono-cycloparaffins are hydrocarbons of type 0; di-olefins, cyclo-olefins, bi-cycloparaffins, and acetylenes are hydrocarbons of type -2. Figure 7 indicates some of the classes of compounds that are possible for the various hydrocarbon types. For simplicity and clarity all cycloparaffins are shown as five membered rings.

FIG. 7 POSSIBLE CLASSES OF COMPOUNDS IN "ULTRASENE"

Preliminary assignment for classes of compounds in the identified hydrocarbon types were made on the basis of the work of a number of previous investigators.^(3,8-11) Infrared and ultraviolet spectrophotometry and gas-liquid chromatography (GLC) were employed in confirmatory tests.

Hydrocarbon type +2 is paraffinic and predominantly n-paraffins as shown by GLC.

The elution characteristics of hydrocarbon types 0, -2 and -4, as shown in Figures 4-6, indicate the cycloparaffinic rather than olefinic nature of these types, while the bromine number for "Ultrasene" of 0.08 ± 0.08 g Br₂/100 g sample (95% confidence limit) confirmed a very low olefin content. With the column conditions employed, cycloparaffins were eluted with paraffins while olefins were separated from both paraffins and cycloparaffins.

The aromaticity of the five hydrocarbon types -6 through -14 was indicated by the elution characteristics, show in Figures 3-6, and refractive indices, Figure 1. Aromatic hydrocarbons were eluted from the silica gel column after paraffins. The refractive indices of chromatographic fractions 17-25 agree well with expected values for mono-nuclear aromatics while the increase of refractive index for fractions 27-29 corresponds to elution of di-nuclear and poly-nuclear aromatics.

Alkyl-substituted benzenes and indans were identified by ultraviolet and infrared spectrophotometric techniques and corresponded to hydrocarbon types -6 and -8, respectively.

Alkyl-naphthalenes were confirmed as type -12 by ultraviolet absorption spectrophotometry and gas-liquid chromatography of fraction 28.

Hydrocarbon types -10 and -14 were tentatively identified as alkyl-substituted indenenes and acenaphthenes on the basis of observed elution characteristics and recently published information about the composition of petroleum.⁽¹²⁾

The concentrations of hydrocarbon types in the aromatic concentrate were estimated from the data and were normalized to the total aromatic content of the sample (3.0 vol %). Mass spectrometric sensitivities were determined experimentally for a series of C₁₀ NBS certified hydrocarbons, and sensitivity data from the current literature^(6,11,12) were utilized as needed. The resultant composition of this lot of "Ultrasene" is shown in Table III. Other lots of "Ultrasene" have contained as little as 0.5 vol % aromatics but none of these were examined by LIVMS.

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Table III

Composition of "Ultrasene"

Component	Concentration, vol %
<u>Aromatics</u>	
Benzenes	1.8
Indans	1.1
Indenes	0.02
Naphthalenes	0.1
Acenaphthenes	<0.01
<u>Non-Aromatics</u>	
Paraffins	} 97.0 (by difference)
Cycloparaffins	
Polycycloparaffins	

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