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C$_9$ and C$_{10}$ Alkylbenzenes and Aromatic Olefins in the Products of the Thermal Aromatization of Naphtha

E. GIL-AV, J. SHABTÁI, I. MICHAELI, R. SCHNURMANN,[1] and E. KENDRICK[1]
The Weizmann Institute of Science, Rehovoth, Israel

In a series of papers published in 1951 Weizmann and others (*12*) discussed the composition of products and the mechanism of thermal aromatizing of hydrocarbon oils by the Catarole process. At that time some fractions had been studied in detail, whereas others had not yet been investigated. The present results concern the composition of a cut distilling between 150° and 190°C.

The yield of this fraction depends on the nature of the charge stock (*11*) and amounts to between 5 and 8% for the type of raw material from which the cut considered in this study was obtained. Its proportion of aromatic olefins (indene, methylindenes, and alkylstyrenes) adds up to a total of 30 to 40%. Other constituents are C$_9$ and C$_{10}$ alkylbenzenes, indane, and about 10% of naphthenes and paraffins. However, only the composition of the aromatic portion is considered here. The study of the aromatic olefins is of particular interest because very few data on the occurrence of this class of compounds in cracking products are found in the literature, and, from the more practical angle, because they are the raw material for the production of a valuable resin.

Aromatics can be separated by adsorption on silica gel (*6*) from their mixtures with naphthenes and paraffins. The alkylbenzenes of this range can be analyzed accurately by combining infrared spectrophotometry with fractional distillation.

The separation and identification of the aromatic olefins present certain difficulties: They cannot be separated by silica gel chromatography and tend to polymerize when heated over long periods during distillation.

For this reason the individual olefins were determined by an indirect method, using mild catalytic hydrogenation, which without affecting the aromatic rings in the molecules, converted the olefins to the corresponding alkylbenzenes and hydrindenes. The difference of the concentration of alkylbenzenes in the hydrogenated material and in a sample freed of its olefins by polymerization, was then determined. This difference is a measure of the amount of aromatic olefins present in the original cut.

MATERIALS

Two plant products of boiling range 150° to 190°C. were made available to the authors by Petrochemicals, Ltd., Manchester, England. These products had been obtained by cracking of a Middle East naphtha of 150° to 210°C. boiling range, containing 10% of naphthenes and 20% of aromatics. The cracking took place at 680° to 700°C., 30 pounds per square inch of pressure and in about 30 seconds of contact time.

The first product, A, contained 80% of material boiling between 150° and 190°C. It was obtained by atmospheric distillation of the crude cracking product and had lost part of its original olefinic constituents by the heat polymerization which occurred in the still. Hence, the results refer to the composition of the distillate and not to that of the crude material. The bromine number of A was 49, corresponding to about 37% of olefins.

The second product, B, was obtained from A after elimination of the major part of the aromatic olefins by clay polymerization. It amounted to 60% of the original distillation cut and contained essentially all the components of A with saturated side chains. This treatment was carried out at the plant of Petrochemicals, Ltd., in the course of the production of a resin used in the paint industry. The temperature for this process lies slightly above room temperature, and as these conditions are mild, it is assumed that no change other than polymerization of the olefins occurs. This is borne out by the fact that the amount of resin formed approached within a few percent the yield expected from the bromine number of the crude cut. A small amount of unpolymerized olefins, however, always

[1] Present address, Manchester Oil Refinery, Ltd., Manchester, England.

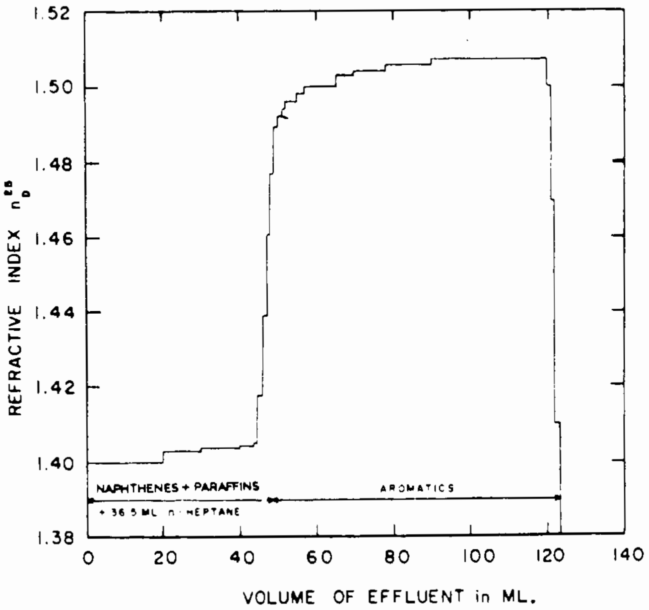

Figure 1. Chromatogram of cut B

remains behind, and accordingly cut B had a bromine number of 7.7, as determined by the method of Francis. However, even after elimination of olefins from this material by 80% sulfuric acid or by hydrogenation, a bromine number of 2 to 4 was still found, apparently caused by substitution (*3*). Thus, only about half of the bromine number of B, corresponding to 2 to 3% of olefins, was due to unsaturation. This small amount was neglected in calculation of the results. No individual olefins except 0.09% of indene and possibly traces of β-methylstyrene were identified in cut B by the infrared spectra.

PROCEDURE

Cut A was hydrogenated, and the resulting product as well as material B was separated into aromatic and naphthenic plus paraffinic portions by chromatography of batches of these materials. The aromatic portions were fractionated on a Podbielniak column, and each fraction was analyzed by infrared spectrophotometry.

Hydrogenation of Aromatic Olefins. Cut A was hydrogenated over Raney nickel at room temperature (28°C.) and at a pressure of 70 pounds per square inch until no more hydrogen was taken up even after addition of fresh catalyst. Under these conditions no saturation of the aromatic rings took place. This is borne out by a comparison of the amount of naphthenes and paraffins in the hydrogenated cut A (9.3%) and the corresponding figure of 8.7% for the original cut A (Table V), as the amount of naphthenes would obviously have been higher in the hydrogenated than in the original fraction if aromatic rings had become saturated. The difference of 0.6% is within the limits of the errors of the method.

Separation and Fractionation of Aromatic Portions. The procedure of Mair (*6*) was followed, to separate the aromatic portions from the hydrogenation product of cut A and from cut B by chromatography of portions of these two cuts on silica gel of 28- to 200-mesh size. As the aromatic content of the materials was above 90%, they were first diluted with heptane. An example of a chromatogram of 86 ml. of B plus 36.5 ml. of heptane is given in Figure 1.

The aromatic portions were then fractionated on a Podbielniak column of 100 plates at a reflux ratio of 100 to 1, and a distillation rate of 2 to 3 ml. per hour. In this way 1100 ml. of hydrogenated A and 1540 ml. of B were each separated into a number of fractions. These materials (see Figures 2 and 3 for boiling ranges) were subjected to infrared analysis. Operational losses during the various stages of separation were distributed equally over all cuts. They amounted to 5% in the case of the chromatographic adsorption, and to 4 and 7%, respectively, for the distillation of B and of hydrogenated A.

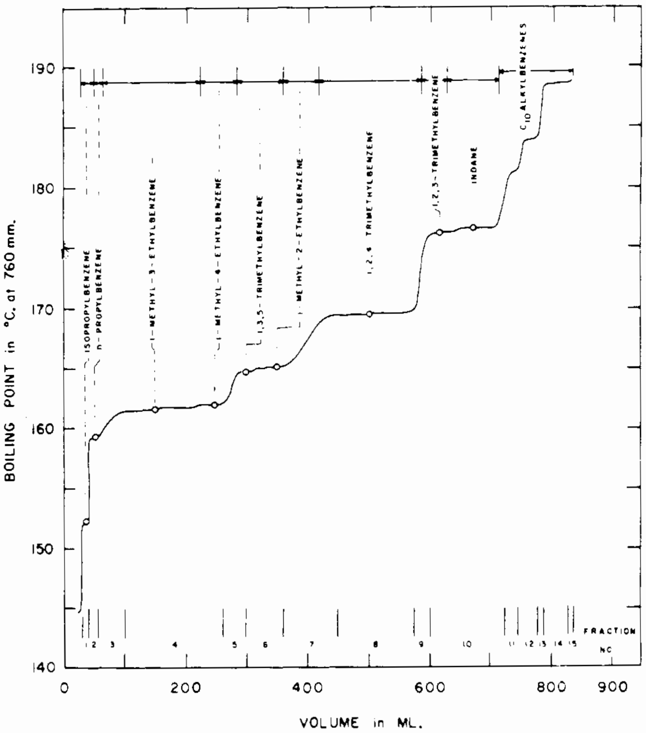

Figure 2. Distillation curve of hydrogenated cut A

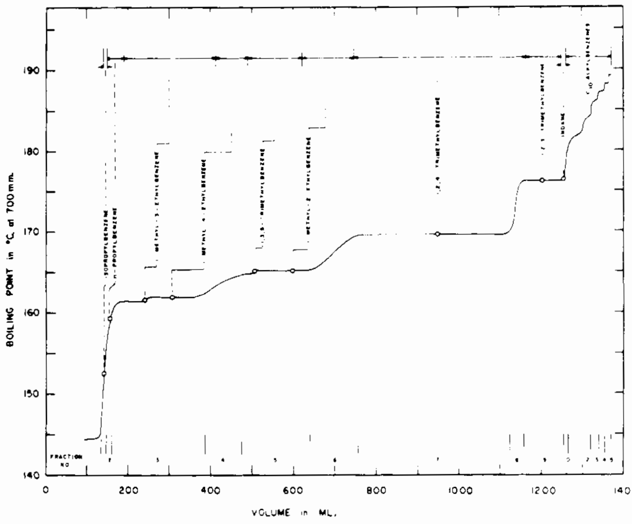

Figure 3. Distillation curve of cut B

Infrared Analysis. The spectra of all distillation fractions of the 150° to 190°C. cut were examined with a Perkin-Elmer Model 21 instrument and evaluated on the basis of measurements made with the same instrument on a series of pure hydrocarbons and in some cases on the basis of coefficients arrived at by estimation (Table I).

Table I. Analytical Wave Lengths and Absorption Intensities of Individual Alkylbenzenes

Compound	Analytical Wave Length, μ	Intensity $\frac{D}{cl}$, Ml./Gram *Mm.*	Source of Sample or Information
Toluene	13.76	418	Nitration toluene
o-Xylene	13.48	$470 + \frac{0.063}{c}$	(*4*)
m-Xylene	13.02	$285 + \frac{0.133}{c}$	(*4*)
p-Xylene	12.62	$387 + \frac{0.067}{c}$	(*4*)
Ethylbenzene	14.36	$151 + \frac{0.133}{c}$	(*4*)
n-Propylbenzene	13.47	96.2	NBS sample
Isopropylbenzene	13.15	185	NBS sample
1-Methyl-2-ethylbenzene	13.26	114	NBS sample
1-Methyl-3-ethylbenzene	12.82	59	NBS sample
1-Methyl-4-ethylbenzene	12.25	150	NBS sample
1,2,3-Trimethylbenzene	13.02	208	NBS sample
1,2,4-Trimethylbenzene	12.38	183	NBS sample
1,3,5-Trimethylbenzene	11.96	185	NBS sample
n-Butylbenzene	13.43	91.5	Prepared at Weizmann Institute
Isobutylbenzene	13.57	165.6	Purified C.P. sample
sec-Butylbenzene	13.17	115.5	Prepared at Weizmann Institute
tert-Butylbenzene	13.11	149.3	Prepared at Weizmann Institute
Indane	13.32	142	Prepared at Weizmann Institute
1-Methyl-2-isopropylbenzene	13.21	About 110	Estimated from (*13*)
1-Methyl-3-isopropylbenzene	12.78	About 130	Estimated from (*13*)
1-Methyl-4-isopropylbenzene	12.24	About 170	Estimated from (*13*)
1,3-Dimethyl-5-ethylbenzene	11.86	167	NBS sample
1-Methyl-2-*n*-propylbenzene	13.42	118	Prepared at Weizmann Institute
1-Methyl-3-*n*-propylbenzene	12.85	68	Prepared at Weizmann Institute
1-Methyl-4-*n*-propylbenzene	12.48	81	Prepared at Weizmann Institute
1,2-Diethylbenzene	13.28	About 170	Estimated
1,3-Diethylbenzene	12.53	About 60	Estimated
1,4-Diethylbenzene	12.07	About 160	Estimated
1,3-Dimethyl-4-ethylbenzene	12.24	About 82.2	Estimated from (*13*)
1,2-Dimethyl-3-ethylbenzene	13.84	About 38	Estimated from (*13*)
1,4-Dimethyl-3-ethylbenzene	12.38	About 95	Estimated from (*13*)
1,3-Dimethyl-2-ethylbenzene	13.05	About 136	Estimated from (*13*)

Table II. Preparation and Properties of Alkylbenzenes

Alkylbenzene	Method of Preparation	Boiling Point at 760 Mm. Hg, °C.	Refractive Index	Infrared Absorption
Indane	Hydrogenation of indene	176–177	$n_D^{25} = 1.536$	Spectrum taken with Perkin-Elmer Model 21 fully agrees with curve of (*1*)
1-Methyl-2-*n*-propylbenzene	Grignard reaction of propionaldehyde with corresponding bromotoluene, followed by dehydration over potassium bisulfate and catalytic hydrogenation.	184.0	$n_D^{20} = 1.4992$	Spectra taken with Perkin-Elmer Model 21 agree with data of (*13*)
1-Methyl-3-*n*-propylbenzene		182.0	$n_D^{25} = 1.4896$	
1-Methyl-4-*n*-propylbenzene		183.5	$n_D^{25} = 1.4890$	

Absorption cells 0.12 and 0.24 mm. thick were used and the concentration of solutions of the samples in carbon disulfide was adjusted to bring the principal absorption maxima within the optimum transmittance range of 25 to 50%. Where pure materials were available for calibration purposes (Table I) considerably higher absorption coefficients were found than those reported by Williams, Hastings, and Anderson (*13*), because narrower slits were used (slit program 3—i.e., a variation between 0.2 and 0.4 mm. over the wave length range from 12.0 to 14.35 microns).

The concentrations of the major components of the various distillation fractions were determined from the spectra by using simultaneous equations and applying for the setting up of these equations the corrections described elsewhere (*7*). Components with concentrations of less than 10% were determined by the "base-line" method.

Indane, 1-methyl-2-*n*-propylbenzene, 1-methyl-3-*n*-propylbenzene, and 1-methyl-4-*n*-propylbenzene were synthesized by the methods indicated in Table II. Wherever possible, the intermediate products of the synthesis were carefully purified by crystallization or fractionation. The final products were fractionated on a column of about 50 theoretical plates.

Among the dimethylethylbenzenes the only one which was available for the taking of its reference spectrum was 1,3-dimethyl-5-ethylbenzene. The absorption coefficients of the diethylbenzene isomers were estimated from the spectra of two mixtures of isomers, one of which contained mainly *m*- and *p*- compounds and the other *o*- and *p*-diethylbenzene. The integrated absorption intensities of the out-of-plane C-H bending vibrations were compared with those of similar alkylbenzenes whose spectra are known. The coefficients estimated in this manner should be reliable to ± 10%.

RESULTS

The results of the infrared analyses of the various fractions are given in Tables III and IV. Table V contains the composition of hydrogenated cut A and of cut B as calculated from the infrared data and the volume of each fraction. Multiplication by 0.6 of the figures for cut B gave the composition of the original cut A (see column 3, Table

Table III. Composition of Hydrogenated Cut A
(For distillation curve see Figure 2)

	Fraction Number																	
	1	2	3a[a]	3b[a]	4	5	6	7	8	9	10a[a]	10b[a]	10c[a]	11	12[b]	13[c]	14[d]	15
	Component, Weight Per Cent																	
o-Xylene	3.5																	
Styrene	...																	
Isopropylbenzene	53.0	13.4	1.9															
n-Propylbenzene	42.0	21.1	24.1	20.8														
1-Methyl-3-ethylbenzene	...	32.3	46.0	58.6	75.5	21.7	Trace											
1-Methyl-4-ethylbenzene	1.1	7.4	13.6	10.9	24.4	22.0	7.0											
1,3,5-Trimethylbenzene	0.3	0.5	0.8	0.6	5.4	33.6	59.9	22.0	Trace									
1-Methyl-2-ethylbenzene				Trace	10.7	21.5	44.7	24.2	0.2									
1,2,4-Trimethylbenzene							Trace	50.5	91.0	28.7	Trace							
1,2,3-Trimethylbenzene									0.3	39.8	51.2	40.0	11.9	5.5				
Indane										13.5	29.0	41.2	81.0	19.4				
1-Methyl-4-isopropylbenzene										Trace	11.7	4.2	2.3	...				
1-Methyl-3-isopropylbenzene												5.4	0.8	...				
1,3-Diethylbenzene													2.2	18.2				
1-Methyl-3-*n*-propylbenzene														12.3				
Indene														Trace				
1,2-Diethylbenzene														...	3.6	0.5	4.2	1.7
1,3-Dimethyl-5-ethylbenzene													0.7	8.0	39.2	12.8	1.7	1.3
1,4-Diethylbenzene												0.3	0.7	1.0	3.4	Trace		
Total	99.9	74.7	86.4	90.9	116.0	98.8	111.6	96.7	91.5	82.0	91.9	91.1	99.6					
Fractions, vol. % on total cut	1.3	1.8	2.2	3.5	20.3	4.7	7.3	11.3	15.4	3.3	2.6	3.8	8.8	2.6	3.9	1.1	5.2	0.9

[a] Fraction 3 subdivided into two consecutive subfractions, a and b. Fraction 10 was subdivided into three consecutive subfractions.
[b] Presence of 1,4-dimethyl-2-ethylbenzene and 1,3-dimethyl-2-ethylbenzene was established qualitatively.
[c] Fraction 13 contained bands due to 1,3-dimethyl-2-ethylbenzene, 1,4-dimethyl-2-ethylbenzene, 1-methylindane, and 2-methylindane.
[d] Fraction 14 contained bands due to 1-methylindane and 2-methylindane.

Table IV. Composition of Cut B
(For distillation curve see Figure 3)

	Fraction Number																	
	1	2	3a[a]	3b[a]	4	5	6	7a[a]	7b[a]	8	9a[a]	9b[a]	10	11	12	13	14[b]	15[b]
	Component, Weight Per Cent																	
o-Xylene	9.2																	
Styrene	1.2																	
Isopropylbenzene	52.2	14.6																
n-Propylbenzene	37.4	48.7	17.0															
1-Methyl-3-ethylbenzene		32.3	76.0	73.0	34.0													
1-Methyl-4-ethylbenzene		5.4	17.0	34.0	29.0	1.1												
1,3,5-Trimethylbenzene		0.2	4.0	8.5	31.0	30.7	35.0	0.5										
1-Methyl-2-ethylbenzene					8.0	56.5	20.2	...										
1,2,4-Trimethylbenzene						2.5	43.0	97.8	84.2	48.1	0.2							
1,2,3-Trimethylbenzene								0.2	0.4	30.3	74.6	80.5	49.1	21.7	1.2			
Indane												11.9	33.0	23.9	Trace			
1-Methyl-4-isopropylbenzene											1.7	2.1	1.7					
1-Methyl-3-isopropylbenzene																		
1,3-Diethylbenzene														2.0	4.0			
1-Methyl-3-*n*-propylbenzene														5.7	24.4	11.0		
1-Methyl-2-*n*-propylbenzene																7.0		
Indene														9.4	13.0			
1,2-Diethylbenzene															Trace	Trace		
1,3-Dimethyl-5-ethylbenzene													1.3	27.4	58.8	41.9	32	13
1,4-Diethylbenzene															1.4	1.2		
Total	100.0	101.2	114.0	115.5	102.0	90.8	98.2	98.5	84.6	78.4	76.5	94.5	85.1	90.1	102.8			
Fraction, Vol. % on total cut	0.8	1.2	13.1	6.3	6.4	13.5	9.2	19.0	11.4	3.1	3.0	3.8	0.7	3.2	1.3	1.8	1.0	1.2

[a] Fractions 3, 7 and 9 subdivided into two consecutive subfractions each.
[b] Fractions 14 and 15 contained bands due to 1,3-dimethyl-4-ethylbenzene, 1,4-dimethyl-2-ethylbenzene; 1,3-dimethyl-2-ethylbenzene, 1-methylindane, and 2-methylindane.

V). The amounts of the aromatic olefins were obtained by subtracting the values in column 3 from those in column 2.

Altogether 65% of the distillation cut has been accounted for by 30 individual compounds. Within the limits of the accuracy of the method most of the C_9 and C_{10} aromatics of the boiling range from 150° to 190°C. were found. However,

1. No butylbenzenes were detected.
2. In the propyl- and isopropylbenzene group the following compounds seem to be absent or else to occur in very small amounts: propenylbenzenes (*β*-methylstyrene), o-methylpropenylbenzene, *m*-methylpropenylbenzene, *p*-methylpropenylbenzene, *o*-methyl-isopropenylbenzene, *p*-methylpropylbenzene, and *m*-methylisopropylbenzene.

The methylhydrindenes and the dimethylethylbenzenes (with the exception of 1,3-dimethyl-5-ethylbenzene) were not measured quantitatively, because of lack of reference data. However, the infrared spectra of the relevant distillation fractions showed absorption bands of all the possible isomers.

The distribution of the individual compounds is such that:

The C_9 aromatics constitute 61% by volume of the cut. Each compound (with the exception of isopropylbenzene and *o*-methylstyrene) is present in relatively large amounts (1.5 to 16%).

The C_{10} aromatics account for 11% by volume of the cut. In this group 1,3-dimethyl-5-ethylbenzene predominates with 1.2%.

Table V. Composition of 150° to 190° C. Distillation Cut[a]

Component	A (Hydrogenated), Vol. %	A (Original Cut), Alkylbenzenes, Vol. % (from B)	A (Original Cut), Olefins, Vol. % (by Difference)	Corresponding Olefin
Isopropylbenzene	0.9	0.3	0.6	α-Methylstyrene
n-Propylbenzene	1.3	1.5		β-Methylstyrene
1-Methyl-2-ethylbenzene	6.3	4.6	1.7	*o*-Methylstyrene
1-Methyl-3-ethylbenzene	15.0	8.3	6.7	*m*-Methylstyrene
1-Methyl-4-ethylbenzene	5.5	3.1	2.4	*p*-Methylstyrene
1,3,5-Trimethylbenzene	7.2	4.9		
1,2,3-Trimethylbenzene	4.1	3.2		
1,2,4-Trimethylbenzene	15.6	15.9		
Indane	7.9	0.4	7.5	Indene
Indene		0.09		
1-Methyl-2-*n*-propylbenzene	...	0.04		
1-Methyl-3-*n*-propylbenzene	0.25	0.2	0.05	*m*-Methylpropenylbenzene
1-Methyl-3-isopropylbenzene	0.2	0.0	0.2	*m*-Methylisopropenylbenzene
1-Methyl-4-isopropylbenzene	0.5	0.07	0.43	*p*-Methylisopropenylbenzene
1,2-Diethylbenzene	0.3	0.0	0.3	*o*-Ethylstyrene
1,3-Diethylbenzene	0.5	0.03	0.47	*m*-Ethylstyrene
1,4-Diethylbenzene	0.2	0.02	0.18	*p*-Ethylstyrene
1,3-Dimethyl-5-ethylbenzene	1.7	1.2	0.5	3,5-Dimethylstyrene
Dimethyl-ethylbenzenes (other than 1,3-dimethyl-5-ethylbenzene) Methylhydrindenes	6.5	1.9	4.6	Dimethylstyrenes, Methylindenes
Distillation residue	15.0	5.4	9.6	
Naphthenes plus paraffins	9.3	8.7		
Total	98.3	59.9	35.2	

[a] Analytical data revised, with small alterations of figures, after presentation at Congress.

Table VI. Comparison of Calculated Equilibrium Concentrations (8) of C_9H_{12} Alkylbenzenes with Values Found Experimentally

Component	Calcd. Mole Fractions at 700° C.	Mole Fractions Found in 150° to 190° C. Cut
1,2,4-Trimethylbenzene	0.30	0.37
1,3,5-Trimethylbenzene	0.09	0.11
1,2,3-Trimethylbenzene	0.09	0.08
1-Methyl-4-ethylbenzene	0.13	0.07
1-Methy--3-ethylbenzene	0.22	0.20
1-Methyl-2-ethylbenzene	0.10	0.11
n-Propylbenzene	0.05	0.04
Isopropylbenzene	0.02	0.01

Table VII. Comparison of Calculated Equilibrium Concentrations (5) of *o*-, *m*-, and *p*-Methylstyrenes with Values Found Experimentally

Compound	Calculated Mole Fraction at 700° C.	Mole Fractions Found in the 150° to 190° C. Cut
o-Methylstyrene	0.18	0.16
m-Methylstyrene	0.53	0.62
p-Methylstyrene	0.29	0.22

None of the others contributes more than 0.5%. The methylhydrindenes and the high boiling dimethylethylbenzenes were not determined individually.

If only the olefins are considered, it appears that about 50% of them are formed by C_9 compounds which are predominantly *m*-methylstyrene and indene. The C_{10} compounds account for 22.5%, 18% of which are dimethylstyrenes and methylindenes. The remaining 27.5% boil above 190°C. and have not been identified. From these data important conclusions can be reached as to the nature of the resin formed from the crude cut by polymerization.

There is remarkably good agreement between the experimentally found concentrations of the C_9H_{12} alkylbenzenes and thermal equilibrium concentrations calculated by Taylor, Wagman, Williams, Pitzer, and Rossini (*8*) for 700°C. (Table VI). A number of similar observations on both crude oils and cracked products have been reported by other authors (*2*, *9*).

DISCUSSION

The random errors normally encountered with the particular infrared spectrophotometer used by the authors are of the order of ±0.5% in transmittance with corresponding errors in absorbance of ±3%.

The analytical wave lengths were chosen so as to avoid overlapping wherever possible. Yet in some cases the errors may exceed ±3%, and thus the total concentrations would be expected to lie between 95 and 105%. Some fractions show a total alkylbenzene content of less than 90% (see Tables III and IV), presumably owing to the presence of saturated hydrocarbons. The totals of four of the fractions which contain appreciable proportions of methylethylbenzene add up to more than 110%. It seemed reasonable to assume that in these cases the coefficients for the methylethylbenzenes (see Table I) were too small, and this was confirmed for 1-methyl-3-ethylbenzene for which a sample of new material yielded $D/cl = 69.5$ as against 59 as given in Table I. With this revision the totals of fractions 4 and 6 of hydrogenated cut A amount to 106.3 and 108.1%, respectively, and the totals of fractions 3a and 3b of cut B are 101.2 and 104.8%, respectively. It was confirmed that revised values for 1-methyl-2-ethylbenzene, 1-methyl-4-ethylbenzene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene (136.7, 142.8, 185.8, and 172.2, respectively) did not materially affect the results. The effect of this revision on the assessment of olefins is that the proportions of *o*- and *m*-methylstyrene would be 1.5 and 5.7%, respectively (see Table V), and correspondingly the mole fractions of *m*-methylstyrene and *p*-methylstyrene (see Table VII) would be 0.59 and 0.25, respectively.

The aromatic olefins were determined by difference. There is therefore the inherent inaccuracy of determining small amounts by difference of two quantities of similar magnitude. This method does not enable one to differentiate between isomers such as propenyl- and allylbenzenes because they yield similar hydrogenation products. However, the propenylbenzenes can be expected to be more stable because of their additional resonance energy. The assumption has therefore been made that the presence of allylbenzenes is unlikely.

A priori one would not expect to find agreement with the thermal equilibrium concentrations in the methylstyrene series, because the relative proportions of the compounds might have been altered by polymerization in the still during distillation and also because their determination is by difference of two quantities of similar magnitude. Nevertheless, the proportions actually agree fairly well with the thermodynamic data (*5*) for *o*-, *m*-, and *p*-methylstyrene at 700°C. (Table VII). However, as long as more accurate data are not available, this agreement may be fortuitous. α-Methylstyrene was found in quantities far smaller than expected. The absence of β-methylstyrene is striking. This might be because of its ease of conversion to indane, indene, and chrysene under the conditions of cracking (*10*).

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