Pyrolysis of C₂ and C₃ Hydrocarbons

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LITERATURE on the pyrolysis of light hydrocarbons is extensive (1, 2, 7, 8, 9). It is difficult to compare the results for various hydrocarbons directly because of differences in experimental conditions reported. Variations in the methods of reporting results also add to the confusion.

The primary purpose of this investigation was to obtain data for the pyrolysis of ethylene, ethane, propylene, and propane at a single temperature and over the same contact time range for each hydrocarbon. This has allowed direct comparison of conversions and product distributions. Emphasis was placed on obtaining data for the production of ethylene and aromatics, since these products are of commercial importance. By varying the contact times over a wide range, the maximum yield of ethylene and of aromatics was determined for each hydrocarbon pyrolyzed.

Experimentation Includes Determination of Yields over Wide Range of Contact Times

Apparatus and Procedure. The apparatus consisted essentially of a system for feeding the charge at a constant rate, a Vycor reactor heated by electric furnaces, a series of cold traps for liquid product recovery, and a gas sampling and metering system. A drawing of the apparatus is shown in Figure 1.

When a pure hydrocarbon was pyrolyzed, the feed gas was withdrawn directly from a cylinder and the flow rate controlled with a rotameter. In the case of gas mixtures, a mixture of the desired composition was first made up in a gasholder at atmospheric pressure. The gas was then pumped from the gasholder at a set rate, using a glass-syringe pump. The hydrocarbon charged was passed through a drying tube containing Drierite (CaSO₄) before entering the reactor.

before entering the reactor. In most of the experiments, the reactor used consisted of a 75-cm. \times 22-mm. outside diameter Vycor tube containing a 7-mm. thermocouple well. The tube was supported in a vertical position, with the gas stream entering at the top. Heat was supplied by means of two electric furnaces, one 15 cm. long (preheater) and the other 60 cm. long. The latter was constructed from a heavy aluminum bronze block having a 2.5-cm. bore. The two end sections and the middle section of the block were heated by means of separate resistance-wire windings so that a uniform temperature could be obtained throughout most of the furnace length. The upper section of the reactor tube, which served as a preheater,

was packed with quartz chips and was maintained at a tempera-ture about 200° F. below that in the reaction zone. The gas leaving the preheater was rapidly brought to reaction temperature upon passing through a constricted section of the tube maintained at the reaction temperature. The reaction zone itself, 58 cc. in volume, extended over a 23-cm. length of the reaction tube and was located in the middle section of the larger furnace. The lower section of the reactor tube con-



Figure 1. Laboratory Apparatus for Pyrolysis of Gaseous Hydrocarbons

thermocouples. For those experiments at very long contact times, a larger furnace and a reactor of a volume of about 300 cc. were used. The effluent from the reactor was passed through two cold traps, maintained at 0° C., to remove liquid products. The gas leaving the cold traps was then sampled for mass spectrometer analysis and the remainder passed through a wet test meter.

leaving the cold traps was then sampled for mass spectrometer analysis and the remainder passed through a wet test meter. In order to obtain a representative sample of the off-gas, an automatic sampling system was employed. This system was controlled by the wet test meter in such a way that a predetermined aliquot of gas was collected from each 1.5 liters of off-gas.

tained a close-fitting Vycor plug, so that the products were rapidly removed from the heated zone. The temperature was read

at various points in the furnace block and reactor by means of

In general, the experiments with pure hydrocarbons were carried out on a relatively small scale (approximately 1 gram-mole of gas fed), so that insufficient liquid product was obtained for distillation. Thus, only the total weight of aromatics (C_{6+}) was determined in these cases. In order to obtain information as to the nature of the liquid product, a number of larger scale runs were made under certain selected conditions. For the experiments with gas mixtures, sufficient liquid product was obtained so that a fractionation through light aromatics could be made. In all cases, a mass spectrometer analysis of the noncondensed products was made. Coke formation was determined for each run by passing a slow stream of air through the reactor at 900° F. and absorbing the carbon dioxide formed in Ascarite.

The hydrocarbons pyrolyzed were obtained from The Matheson Co., and were used without further purification. All experiments were at atmospheric pressure.

Experimental Conditions. Most of the experiments were carried out at 1500° F. The discussion of the data will be limited primarily to the results obtained at this temperature. The contact times used at 1500° F. were varied over a wide range, so that for each hydrocarbon charged the maximum yield of both aromatics and ethylene was determined. In addition, a number of experiments were carried out at 1350°, 1400°, and 1650° F. in order to determine the effect of temperature on product yields. Tables of the experimental conditions and yields of products for the pyrolysis of ethylene, ethane, propylene, and propane are available (4).

erally be presented as a function of contact time rather than per cent of charge converted. This was done because, in most cases, the contact times were extended beyond those required for essentially 100% conversion of the gas feed. The contact time is given by the expression, $t = \int_{-\infty}^{t'} \alpha dt'$, where

In the discussion be-

low, the yields will gen-

t =the contact time in

seconds, t' = the nominal contact time obtained by dividing the reactor volume in cc. by the gas feed rate in cc. per second at operating conditions, and $\alpha =$ the ratio of the volume of gas fed to the volume of exit gas at t'. The contact time is evaluated graphically by plotting α as a function of t' for a series of experiments at various gas feed rates.

Selection of Operating Conditions and Charge Stocks Yields Wide Range of Aromatic Products

Pyrolysis of Individual Hydrocarbons at 1500° F. RELATIVE CONVERSIONS. The conversion as a function of contact time for each hydrocarbon pyrolyzed is given by Figure 2. At contact times below about 0.6 second, the rates of conversion are in the order $C_2H_4 < C_3H_5 < C_2H_5 < C_3H_5$. The rate for ethane falls off rapidly, so that at longer contact times it is intermediate between the rates for ethylene and propylene. Essentially complete conversion (>99%) of propylene and propane is obtained in 3 to 5 seconds. With ethylene and ethane, however, conversions of only about 95% have been reached at 25 to 30 seconds contact time.

YIELDS OF AROMATICS. The yields of total aromatics (C_{6+}) as a function of contact time are given by Figure 3. At the lower contact times, only very small yields are obtained from ethane and propane. As the contact time is increased, the yields increase until a maximum of 25 to 30 weight % for both ethane and propane is reached. When ethylene or propylene is pyrolyzed, much higher yields are obtained, even at relatively low contact times. Yields of aromatics of over 40 weight % from propylene and over 50 weight % from ethylene were realized. The reaction conditions and yields for maximum aromatics formation at 1500° F. are as follows:

Charge	Contact	Conver-	Aromatics Yield,
	Time,	sion,	Wt. % of Charge
	Sec.	%	Converted
Ethylene Ethane Propylene Propane	$3.5 \\ 19.0 \\ 7.0 \\ 13.0$	${}^{68}_{95}_{\sim 100}_{\sim 100}$	56 28 43 28

YIELD OF ETHYLENE. The yields of ethylene as a function of contact time are given by Figure 4. From ethane, yields of 85 to 90 weight % were obtained at short contact times and conversion levels below about 50%. As the contact time is increased, the ethylene yield falls off rapidly. With propylene and propane, the yields are fairly constant over a considerable range at the lower contact times, being about 30 weight % for propylene and 40 to 45 weight % for propane. The reaction conditions and yields for maximum ethylene production at 1500° F. are shown below:

Charge	Contact Time, Sec.	Conver- sion, %	Ethylene Yield, Wt. % of Charge Converted
Ethane	0.18	43	88
Propylene	0.50	66	30
Propane	0.50	93	45

YIELD OF METHANE. The methane yields from each hydrocarbon pyrolyzed are shown as a function of contact time in Figure 5. The methane formed, which represents a major component of the product in each case, increases regularly with increasing contact time. At the longest contact times used, the methane yields are from 30 to 35 weight % for ethylene and propylene, and about 50 weight % for ethane and propane.

OTHER C_2 TO C_5 HYDROCARBONS. In addition to methane and ethylene, considerable amounts of other light hydrocarbons are usually formed at the lower contact times. These light hydrocarbons consist of paraffins, olefins, and diolefins in the C_2 to C_5 range. The total yields of products in this range (exclusive of ethylene and the hydrocarbon charged) are given by Figure 6.



Figure 2. Effect of Contact Time on Conversion of Light Hydrocarbons at 1500° F.



Figure 3. Yields of Aromatics (C_{6+}) at 1500° F.



Figure 4. Yields of Ethylene at 1500° F.



Figure 5. Yields of Methane at 1500° F.



Figure 6. Yields of C_2 to C_5 Hydrocarbons (Exclusive of Ethylene) at 1500° F.



Figure 7. Yields of Propylene and Diolefins at 1500° F.

From the pyrolysis of ethylene, this intermediate fraction consists mainly of ethane, propylene, and butadiene. With propylene, the chief constituents are butadiene, butene, and pentadiene. Propylene is the main product in this range when propane is pyrolyzed. The yields of some of the more important components of this fraction are given by Figure 7.

COKE. The coke yields as a function of contact time are shown by Figure 8. In the lower contact time range, the coke formed from each hydrocarbon charged represents less than 5 weight % of the product. The amount of coke formed rises as the contact time is increased, ranging from about 10 weight % for ethane to over 25 weight % for ethylene at the longest contact times used.

Effect of Temperature on Product Yields. In addition to the experiments made at 1500° F., several were carried out with ethane at 1400° F., with propylene at 1350° and 1650° F., and with ethylene at 1650° F. Comparing yields at fixed conversions, the yield of ethylene from both ethane and propylene increased with increasing temperature in the range investigated. The yield of aromatics from propylene was somewhat higher at 1350° than at 1500° F. With ethylene, a slightly higher yield of aromatics was obtained at 1650° than at 1500° F. The effect of temperature on the yields of ethylene and aromatics is shown by Figures 9 and 10.

Effect of Promoters on Conversion. The effect of free radical reaction-initiators on the rate of pyrolysis of ethane and propylene was investigated. From 4 to 6 mole % of dimethyl disulfide or

1,2-dichloroethane was added to the hydrocarbon charge stream. The conversion was compared to that obtained without promoter at the same temperature and space velocity. Table I gives the results for several experiments in which promoter was used. With propylene, an increase in conversion of 20 to 50% was obtained at conversion levels below about 40%. At higher conversion levels, the promoter had no effect. With ethane, an increase in conversion of only 5% or less resulted when dimethyl disulfide was added to the charge stream. The difference between propylene and ethane in promoter effect probably is due to the difference in the C—H bond strengths for the two hydrocarbons. The C—H bond strength of the methyl group in propylene is about 20 kcal, weaker than that for ethane. Propylene should therefore be more susceptible to free radical attack.

Table 1. Effect of Promoters on Conversion of Propylene and Ethane

Hydro-	Catalyst			Space	Convers	sion, %
carbon Charged	Type	$\stackrel{ m Mole}{\%}$	Temp., ° F.	Velocity ^a , Hr. ⁻¹	Without Catalyst	With Catalyst
Propylene	Dimethyl disulfide	4	$1350 \\ 1350 \\ 1500 \\ 1000 \\ $	$977 \\ 436 \\ 2520 \\ 1500$	$16 \\ 34 \\ 47 \\ 64$	$24 \\ 41 \\ 47 \\ 69$
Propylene	1,2-Dichloro- ethane	4	1350 1350 1350	946 422	04 16 35	02 21 44
Ethane	Dimethyl disulfide	6	$1400 \\ 1400 \\ 1500 \\ 1500 $	$1700 \\ 739 \\ 3100 \\ 1730$	$21 \\ 35 \\ 47 \\ 62$	$22 \\ 36 \\ 46 \\ 64$

^a Volumes of gas fed at S.T.P./hour/volume of reactor.

Pyrolysis of Gas Mixtures. Mixtures of light hydrocarbons were pyrolyzed at 1500° F. The feed compositions used were designed to be typical of refinery gas streams available for the production of ethylene or aromatics. For this reason, isobutane





Figure 9. Effect of Temperature on Yield of Ethylene



Figure 10. Effect of Temperature on Yield of Aromatics (C_{ϵ^+})

and n-butane were added to the feed in some cases. The composition of the mixtures fed, reaction conditions, and product yields are given in Table II. In experiments 1, 2, and 3, mixtures of the same composition were pyrolyzed at different contact times. An aromatics yield of 25 to 30 weight % of the gas fed was obtained over the contact time range of about 6 to 20 seconds. The ethylene yield ranged from about 43 weight % at 1.6 seconds down to about 10% at 20 seconds.

Table II. Experimental Conditions and Results for Pyrolysis of Gas Mixtures at 1500° F.

		Expe	rinent	No.	
	1	2	3	4	5
Space velocity ^a , hr. ⁻¹ Contact time, sec.	$\substack{334\\1.6}$	75.0 6.6	$^{252}_{192}$	$\substack{78.3\\6.5}$	$\begin{array}{c} 80.0 \\ 6.5 \end{array}$
Composition of feed, wt. 76 Ethylene Ethane Propylene Propylene	$8.7 \\ 23.8 \\ 7.6 \\ 42.7$	$7.0 \\ 24.3 \\ 8.4 \\ 43.2$	7.2 24.2 8.4 42.5	$10.0 \\ 28.7 \\ 10.3 \\ 51.0$	$25.6 \\ 29.9 \\ 7.5 \\ 37.0$
Isobutane Butane Total	$7.0 \\ 10.2 \\ \overline{100.0}$	$ \begin{array}{r} 6.6 \\ 10.5 \\ \overline{100.0} \end{array} $	$7.2 \\ 10.4 \\ 100.0$	100.0	100.0
Yield of products, wt. % of gas fed Hydrogen Methane Coke Ethylene Ethylene Propylene Propylene Cr-Cs Light aromatics (Co-Cs) Heavy aromatics Total	$\begin{array}{r} 2.2\\ 26.5\\ 2.5\\ 42.6\\ 7.9\\ 3.0\\ 0.4\\ 1.5\\ 7.5\\ 5.9\\ 100.0 \end{array}$	2.634.04.324.74.81.00.21.810.416.2100.0	$\begin{array}{r} 3.1 \\ 40.5 \\ 13.5 \\ 10.8 \\ 2.9 \\ 0.5 \\ 0.2 \\ 0.7 \\ 9.7 \\ 18.1 \\ 100.0 \end{array}$	3.0 33.1 4.5 $5.84.52.25.897162100.0$	$\begin{array}{r} 2.9\\ 29.8\\ 7.8\\ 26.0\\ 5.2\\ 0.3\\ 0.2\\ 2.2\\ 25.9\\ \hline 100.0 \end{array}$
^a Volumes of gas fed at S.T.P./ho	ur/volun	ne of rea	ctor.		

In experiments 4 and 5, the gas fed consisted only of C_2 and C_3 hydrocarbons. Also, in experiment 5, a relatively high proportion of ethylene was used in the charge in order to simulate ethylene-recycle conditions. The results for experiments 2, 4, and 5 show that essentially the same product yields were obtained in each case, even though the feed compositions were considerably different.

The yields for experiments 4 and 5 can be compared with those predicted from the data obtained for the pyrolysis of each component alone. The comparison of actual and predicted yields is as follows:

	Yield, Wt.	% of Gas Fed	Yield, Wt. %	of Gas Fed
Product	Predicted	Actual (expt. 4)	Predicted	Actual (expt. 5)
Ethylene Aromatics	$\begin{array}{c} 24.1 \\ 27.7 \end{array}$	$\begin{array}{c} 25.3 \\ 25.9 \end{array}$	$\begin{array}{c} 23.6\\ 29.8 \end{array}$	$egin{array}{c} 26.0\ 25.6 \end{array}$

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The yields of ethylene are slightly higher and the yields of aromatics slightly lower than the predicted values. This is explained on the basis of a reduction in the rate of conversion of ethylene to aromatics due to the presence of a high concentration of paraffins. This effect will be further described.

Composition of Aromatics Fraction. The C_{θ^+} fraction obtained in the pyrolysis of ethylene, ethane, propylene, propane, or gas mixtures consists of aromatic hydrocarbons ranging from benzene to highly condensed ring systems. At reaction conditions resulting in the maximum yield of aromatics, the composition of the aromatics fraction is generally the same for each hydrocarbon charged. The product is approximately 40 weight % monocyclic aromatics, 20 weight % dicyclic aromatics, 10 weight % tricyclic aromatics, and 30 weight % heavy residue. Table III shows the composition of the C₆₊ fractions for the pyrolysis of individual hydrocarbons under conditions giving maximum aromatics production. Mass spectrometer analysis of the light aromatics fraction (C_6 to C_8) for the experiments with ethylene and propylene has shown the completely aromatic nature of the product. In these two cases, the C₆ to C₈ fraction consisted of about 85 weight % benzene, 8 weight % toluene, 3 to 7 weight % styrene, and traces of ethylbenzene and xylene. The dicyclic aromatics fractions recovered by distillation were solids having an oily appearance. These fractions were combined and the naphthalene content determined by recrystallization from methanol. The combined fractions contained 75 weight % naphthalene and 25 weight % of liquid material which was assumed to be methylnaphthalenes. Recrystallization of the combined tricyclics fractions gave 85% solid product and 15% oil. The nature of the higher boiling residue was not investigated.

While products of the same general nature were obtained in the experiments discussed above (Table III), certain differences in product distribution do exist. For example, both the ratio of light to heavy aromatics and the ratio of benzene to C_7 and C_8 aromatics vary somewhat from experiment to experiment. It might be expected that the composition of the aromatics fraction would depend upon both the hydrocarbon pyrolyzed and the reaction conditions used. Table IV gives the ratio of light to heavy aromatics and of benzene to C_7 and C_8 aromatics for experiments at 1500° F. For gas mixtures and propylene, results were obtained at more than one contact time. These results show that the ratio of light to heavy aromatics decreases as contact time is increased, while the ratio of benzene to C₇ and C₈ aromatics increases. In Figure 11, the ratios of light to heavy aromatics for experiments with gas mixtures (experiments 1 to 3, Table II) have been plotted as a function of contact time and a smooth curve drawn through the points. Also included in Figure

Table III.	Composition	of	Aromatics	(C ₆₊)	Fraction	from
Pyrolysis of	Light Hydroco	arb	ons at 1500)° F. ur	ider Conc	litions
1 1	of Maximur	n A	romatics Fo	ormatic	m	

	Hydrocarbon Charged			
	Ethylene	Ethane	Propylene	Propane
Space velocity ^a , hr. ⁻¹ Contact time, sec. Conversion. %	$288.0 \\ 3.20 \\ 67$	$27.4 \\ 19.2 \\ 95$	$^{86.5}_{7.15}$	$^{22.9}_{18.5}_{\sim 100}$
Aromatics yield, wt. % of charge converted Composition of aromatics frac-	54	27	42	28
tion, wt. % Cs (benzene) C7 (toluene)	38.5 4.2	39.6	30.5 3.1	$\begin{array}{c} 35.7 \\ 1.9 \end{array}$
Ca (xylene, styrene, etnylden- zene)	4.05	1.4	1.80	1.0
Total light aromatics Crude naphthalened Tricyclics Residue	$ \begin{array}{r} 46.7 \\ 18.0 \\ 10.3 \\ 25.0 \\ \end{array} $	$\begin{array}{r} 42.5 \\ 19.9 \\ 13.7 \\ 23.9 \end{array}$	$35.4 \\ 19.7 \\ 11.3 \\ 33.6$	$38.6 \\ 18.8 \\ 11.8 \\ 30.8 $
Total heavy aromatics	53.3	57.5	64.6	61.4

^a Volumes of gas fed at S.T.P./hour/volume of reactor.
^b C₆ cut is 6 wt. % xylene, 22 wt. % ethylbenzene, and 72 wt. % styrene.
^c C₅ cut is 4 wt. % xylene, 9 wt. % ethylbenzene, and 87 wt. % styrene.
^d Recrystallization of combined crude naphthalene fractions from these four experiments gave 75% naphthalene and 25% oil (methylnaphthalenes).

11 are similar ratios for individual hydrocarbons. The points for the individual hydrocarbons fall on or near the curve for the gas mixture experiments. The values for the ratio of benzene to C_T and C_s aromatics have been plotted in the same way in Figure 12. The points for the individual hydrocarbons again fall on or near the curve for the experiments with gas mixtures. These results



Figure 11. Effect of Contact Time on Ratio of C_5 to C_3 Aromatics to Heavy Aromatics at 1500° F.



show that the distribution of aromatics tends to be largely a function of the severity of reaction conditions (contact time) and is independent of the hydrocarbon pyrolyzed. This suggests that essentially the same mechanism for aromatics formation may be operative for each hydrocarbon.

Table IV.	Effect of Contact Time on Distribution of Aromatics
	for Pyrolysis at 1500° F.

Gas Fed	Contact Time, Sec.	Ce-Cs Aromatics/ Heavy Aromatics ^a	Benzene/Cr-Cs Aromaticsª
Mixture ^b Mixture ^b Ethylene Ethane Propylene Propylene Propane	1.6 6.6 19.2 3.20 19.2 0.53 7.15 18.5	$\begin{array}{c} 1.26 \\ 0.64 \\ 0.53 \\ 0.87 \\ 0.74 \\ 3.90 \\ 0.55 \\ 0.63 \end{array}$	$\begin{array}{c} 3.4 \\ 7.4 \\ 12.3 \\ 4.7 \\ 13.7 \\ 2.7 \\ 6.2 \\ 12.4 \end{array}$
Weight ratio.			

b Composition given in Table II, experiments 1-3.

Theoretical Interpretation of Formation of Aromatics Is Based on Free Radical Mechanism

The pyrolysis of light hydrocarbons involves a series of primary and secondary reactions leading to a complex mixture of products. Figures 13 to 16 show the over-all distribution of products at 1500° F. for each of the hydrocarbons pyrolyzed. Both molecular and free radical processes may be taking place. Therefore, it is difficult to formulate an over-all mechanism for the pyrolysis of any given hydrocarbon. No attempt has been made to develop mechanisms for the over-all pyrolysis reactions. Instead, attention has been centered on the development of a mechanism for the formation of aromatics.

The most generally accepted mechanism for the formation of aromatics is based on the hypothesis originally proposed by Hague and Wheeler (3). It involves a molecular process of the Diels-Alder type of synthesis. For example, it is postulated that butadiene adds to ethylene, forming a compound or complex which loses hydrogen to yield benzene.

$$C_4H_6 + C_2H_4 - - \rightarrow C_6H_{10} - - - - \rightarrow C_6H_8$$

Similarly, styrene would be formed by the dimerization of butadiene and naphthalene by the addition of butadiene to benzene. Schneider and Frolich (δ) questioned the mechanism proposed for the formation of butadiene from ethylene but did not offer an alternative explanation. More recently, Weizmann and coworkers (11) report that the aromatics formed by the pyrolysis of petroleum naphthas can best be explained by the diene synthesis mechanism. Rowley and Steiner (δ) investigated the dimerization of butadiene and the reaction of butadiene and ethylene over the temperature range of 400° to 600° C. They interpret their results as confirming the assumption that the products are formed by molecular association.

A free radical mechanism was used to interpret the experimental data, largely because the relative yields and rates of the formation of aromatics from both paraffins and olefins could be explained more fully than by a molecular mechanism. In the free radical process, it is postulated that the formation of aromatics involves the addition of vinyl radicals to ethylene and propylene, followed by the continued addition to ethylene of radicals derived from the intermediate conjugated olefins and/or aromatics.





It is proposed that ethylene dimerizes in an initiation step, yielding butene which decomposes to form methyl and hydrogen radicals. These radicals extract a hydrogen from ethylene, producing the vinyl radicals.

$$2C_{2}H_{4} - \cdots > C_{4}H_{8} < \checkmark CH_{2} - CHCH = CH_{2} + H \cdot \\ \sim CH_{2} - CH = CH_{2} + CH_{3} \cdot \\ C_{2}H_{4} + H \cdot / CH_{3} - \cdots > C_{2}H_{3} \cdot + H_{2} / CH_{4}$$

The high initial concentration of ethylene favors the extraction reaction even though the C—H bond strength of ethylene is large. As the concentration of olefin decreases, the competing reactions (addition, decomposition, hydrogen extraction) would practically eliminate the vinyl radicals. Thus, the bulk of the aromatics formation must take place during the early stages of the pyrolysis reaction.

In a sense, the intermediate compounds (conjugated olefins and aromatics) serve to propagate the reaction because they form comparatively stable radicals having a sufficiently long life period to afford an opportunity for addition to an ethylene molecule. It is also possible that vinyl radicals may add to butadiene to form higher products.

$$C_{2}H_{4} \xrightarrow{C_{2}H_{3}} C_{4}H_{7} \xrightarrow{C_{2}H_{3}} C_{6}H_{6} \xrightarrow{C_{2}H_{3}} Heavy$$

$$C_{4}H_{6} \xrightarrow{C_{2}H_{3}} C_{6}H_{9} \xrightarrow{C_{6}H_{6}} C_{2}H_{3} \xrightarrow{} products$$

Figure 17 is a simplified diagrammatic flow sheet summarizing some of the most likely reactions for the formation of aromatics from ethylene and propylene. The formation of aromatics is illustrated by both the conjugated olefin route and the aromatic intermediate route. It is likely that hexatriene is the highest molecular weight conjugated olefin that can exist under the reaction conditions. Figure 17 also shows the formation of aromatics from propylene via the allyl radical route.

Certain results that are difficult to explain on the basis of the



Figure 14. Yield of Products from Ethane Pyrolysis at 1500° F.

molecular mechanism can be explained reasonably by the free radical mechanism:

Similarity of aromatic products from the various charge stocks High yield of toluene from the pyrolysis of ethylene

High ratio of benzene to toluene obtained in the pyrolysis of propylene

Faster rate of the formation of aromatics from propylene than from ethylene

Slow rate of the formation of aromatics from the paraffins as compared to the olefins



Figure 15. Yield of Products from Propylene Pyrolysis at 1500° F.



Figure 16. Yield of Products from Propane Pyrolysis at 1500° F.



Figure 17 shows that propylene is formed by the methylation of ethylene, and, conversely, ethylene is obtained by the demethylation of propylene. Similarly, the methylation and demethylation reactions leading to the formation of aromatics make it possible to obtain approximately the same products from either ethylene or propylene.

The comparatively high yield of toluene from ethylene can be explained on the basis of the methylation of butadiene. Demethylation reactions account for the formation of benzene from propylene. In addition to this reaction, the combination of allyl radicals to form diallyl and subsequent cyclization and dehydrogenation result in the formation of benzene.



Figure 18. Rate of Aromatics (C_{6+}) Formation at 1500° F.

Figure 18 compares yields of aromatics for the four hydrocarbons as a function of contact time. The rates of the formation of aromatics are in the order, $C_2H_6< C_3H_8< C_2H_4< C_3H_6$. In the pyrolysis of ethylene and propylene the aromatics form rapidly, reaching their maximum yields at relatively low contact times. The yield of aromatics decreases gradually as the contact time range is extended to 20 seconds. This suggests that in the case of the olefins, the formation of aromatics is closely associated with the primary decomposition products.

The high rate of aromatics formation from propylene is explained on the basis of Szwarc's (10) investigation of the pyrolysis of propylene, in which it was shown that the initial decomposition reaction is the formation of allyl and hydrogen radicals. The allyl radicals combine to form diallyl, which can form benzene by a free radical dehydrogenation process. It is assumed that this process has a faster rate than that involving ethylene, which requires dimerization, decomposition, and hydrogen extraction to form the vinyl radicals.

The formation of aromatics from ethane and propane is comparatively slow, in spite of the fact that high concentrations of olefin are present in the early stages of the pyrolysis reaction (Figures 14 and 16). Assuming that the formation of aromatics is dependent upon the presence of vinyl and allyl radicals, it is necessary to account for their absence or low concentration in the pyrolysis of paraffins. The low concentration of vinyl radicals is attributed to the inhibitory effect of the paraffinic charge stock. Thus, the vinyl radicals do not get a chance to add to ethylene because they are extracting hydrogen primarily from unreacted ethane or propane. As the charge stock becomes more completely converted, the concentrations of the vinyl radicals and polyolefins increase sufficiently to form some aromatics. Figure 16 shows that propylene is formed in the initial stages of the pyrolysis of propane. The faster rate of aromatics formation from propane than from ethane can be explained by assuming that allyl radicals are produced from propylene and combine to form diallyl, which undergoes a free radical cyclization and dehydrogenation to form aromatics.

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