Pyrolysis of Simple Paraffins to Produce Aromatic Oils

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URING recent years there has developed an increased interest in the conversion of hydrocarbon gases into motor fuels. This is mostly due to the growth of a large production of natural gas and refinery vapors without a satisfactory market. Of the possible outlets for products derived from such gases, only the motor-fuel market is large enough to put to use more than a small fraction of the available gas. Of the proposed methods for converting hydrocarbon gases into motor fuel, cracking to produce benzene is perhaps the simplest and has received the most attention. Cracking temperatures above 700° C. are required, and this

introduces practical difficulties not encountered in oil cracking. Methane, in spite of its abundance, offers less promise perhaps at the present time as a source of benzene than the other gaseous hydrocarbons because of the high temperatures needed to decompose it and the low yields of benzene obtained. Fractionator vapors from refineries and gasoline plants, composed chiefly of gaseous hydrocarbons other than methane, are more suitable for conversion into benzene and are available in large quantities.

The pyrolysis of gaseous hydrocarbons other than methane under conditions which produce aromatic hydrocarbons was

first investigated by Berthelot (1) and has since interested a number of investigators. The literature has been recently reviewed by Hurd (13), Hague and Wheeler (11), and Egloff, Schaad, and Lowry (6). Since cracking attained commercial significance, laboratory researches have been conducted by Zanetti (26), Zanetti and Leslie (27), Davidson (4), Williams-Gardner (24), Dunstan (5), Hurd (14), Hague and Wheeler (10, 12), and Wheeler and Wood (23). The utilization of natural gas as a commercial source of benzene has been discussed by Burrell (2). Williamson (25) mentions the operation of a plant for producing benzene from natural gas by pyrolysis. Podbielniak (20) describes semi-large-scale experiments.

The present laboratory investigation was conducted primarily for the purpose of obtaining information bearing on possible commercial operation. The results have also a bearing on coal carbonization and the enrichment of fuel gas by cracking oil, both of which are conducted at temperatures sufficiently high to form benzene.

In the present work more emphasis has been placed on the role of the time factor than in earlier investigations in this field, and a more intimate knowledge of some of the chemical changes involved has been gained by the use of more thorough analytical methods.

Experimental Procedure

Of the gaseous hydrocarbons used in these experiments, ethane, ethylene, propane, and butane were commercial products, containing as impurities other hydrocarbons to the extent of 4 per cent or less. The methane used was natural gas containing 10 per cent of ethane and other impurities. The butane contained 11 per cent of isobutane, and 86 to 88 per cent normal butane. The apparatus used for the cracking operation is shown in Figure 1.

The gas was passed from container A at a uniform rate through flowmeter B and, at atmospheric pressure, into a single straight length of silica tubing, C, which served as the cracking chamber. The silica tube was mounted in a tube furnace, D, so as to slope slightly downward from the horizontal in the direction of flow

The pyrolysis of gaseous hydrocarbons other than methane to produce aromatic oils was studied with emphasis on the part played by the time factor. Maximum yields were obtained over a wide temperature range by using the time of contact appropriate to each temperature. The formation of aromatics took place with evolution of heat. Simple diolefins, chiefly cyclopentadiene, accompanied the benzene in greatest amount during the early stages of its formation.

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of the gases undergoing cracking, in order to allow tar deposited in the exit end of the tube to flow away from the cracking zone. In order to permit time and temperature to be observed separately, a long cracking zone of known volume, maintained at an even temperature, was provided. The tube furnace was 90 cm. in length, wound in three sections controlled by separate rheostats. In this way a 50-cm. cracking zone with a temperature uniform to within 5° C. was obtained. The cracked gases issuing from the tube passed through electric precipitator E, in which the suspended tar was col-lected; through condenser F immersed in a solid carbon dioxideacetone bath to condense the volatile liquid hydrocarbons; and finally into receiver G, or, when large amounts of material were handled, through a wet test meter.

When a run was completed, the volatile liquid hydrocarbons dissolved in the tar in E were distilled into condenser F. This was accomplished by connecting the tar precipitator to the condenser, still immersed in the cooling bath, reducing the pressure to 2 mm. of mercury by a vacuum pump connected to the exit of the condenser, and boiling the tar in the precipitator gently for 10 minutes. The tar volatilized was allowed to condense on the walls of the precipitator while the vapors uncondensed at room temperature were driven over into condenser F. A fractional distillation of the oils had shown that the components boiling between xylene and naphthalene were present in such small amounts under high-yield conditions that the separation of xylene and lower hydrocarbons from the tar was fairly sharp and reproducible.

The tar collected in the tar precipitator was estimated by weighing, and to the weight was added that of the tar deposited in the exit end of the cracking tube. Carbon formed in the cracking zone was determined by burning to carbon dioxide at 550° C. in a stream of oxygen, absorbing in soda lime, and weighing. In most cases the gaseous products were analyzed by means of the Bureau of Mines Precision Orsat apparatus (22). The paraffins, determined by slow combustion, were calculated as methane and ethane. The values for ethane, obtained in this way, may be in error to the extent of 1 per cent or even more.

When a more complete analysis was desired, the gas was separated by fractional distillation into fractions containing methane and gases of lower boiling point—ethane plus ethylene, propane plus propylene, butane plus butene, and liquid hydrocarbons. The gaseous fractions were then analyzed by the Orsat method, olefins being determined by absorption in sulfuric acid, and paraffins by slow combustion. The analytical fractionating column used has been described by Oberfell and Alden (15) Podbielniak (19), and Fitch (7). No attempt was made to determine acetylene, which is known to be formed in small amounts at temperatures high enough to produce arcmatic hydrocarbons.



FIGURE 1. CRACKING APPARATUS

The time of contact was calculated from the volume of the section of the silica tube at cracking temperature and the flow rate of the gas at the temperature of the reaction. A volume increase took place during the reaction, but, since the increase occurred in the brief initial decomposition, the average flow rate was assumed to be that of the products leaving the cracking zone.

During most of the experiments, temperatures were taken only by four thermocouples spaced at equal intervals along the outside of the silica tube. Effects due to heat of reaction caused an appreciable temperature drift during experiments at the higher temperatures, and this, as well as the increased rate of heat transfer, no doubt affected the accuracy of the time and temperature values, especially at the higher temperatures. Such errors are not serious, since the reaction is not responsive to small differences in time and temperature under the conditions which produce aromatic hydrocarbons.

EFFECT OF TIME AND TEMPERATURE

Since other investigators had placed the most emphasis on the temperature factor, it appeared desirable to conduct experiments of an exploratory character to study the effect of independent variation in time as well as temperature. A gas mixture similar to gasoline-plant fractionator vapors of the composition methane 18.6 per cent, propane 44.7 per cent, n-butane 32.7 per cent, and isobutane 4.0 per cent, was cracked at several temperatures—namely, 700°, 750°, 850°, and 950° C.—and propane at 1050° C. Several flow rates were used at each temperature. The results obtained with propane are entirely comparable, as will be shown, with those obtained using the gas mixture, since the average molecular weight and carbon-hydrogen ratio are the same. Because of the wide range of cracking times covered, it was necessary to select silica cracking tubes ranging from 25 mm. diameter for the lower temperatures to 2 mm. for the highest. A simplified type of experiment was deemed adequate in which only the volume change of the gas due to cracking and the concentration of volatile liquid hydrocarbons were determined, for the purpose of calculating the yield of volatile oils (essentially benzene as later experiments show).

The concentration of volatile oils was determined by the method of Burrell (3). The gas discharged from the tar

precipitator was drawn into an evacuated bulb to a final pressure of atmospheric, the inlet stopcock closed, and the bulb was then cooled to -190° C., after which it was brought to -79° C. in an acetone-solid carbon dioxide bath. The uncondensed gases were then withdrawn to a final pressure for 1 mm. The hydrocarbons boiling above room temperature were retained, and the quantity was estimated by warming to room temperature and by reading on an attached manometer the partial pressure of the evaporated residue. The base of the tar precipitator was kept at 60° C. during the cracking operation to avoid condensation of toluene or lower-boiling components, which were not formed in concentrations too high to be retained by the gas. From the volume change due to cracking and the concentration of volatile oils, the yield in weight per cent was calculated.

The yield data are shown graphically in Figure 2. Within this rather wide temperature range the maximum yield was approximately constant for that range of contact time appropriate to each temperature. No doubt the composition of the oils was affected somewhat by temperature. From these data there were selected minimum values of time required to develop a roughly maximum yield of volatile oils within this temperature range. These values are related to the temperature by the following empirical formula:

$$T = 691 - 100 \log t$$

where $T =$ temperature in ° C.
and $t =$ time in minutes

More accurate subsequent experiments confirmed the values selected. The temperature coefficient of reaction rate is distinctly lower than that of the primary decomposition of propane and butane for which Pease (16) found a temperature coefficient of about 2.75 per 25° C. A lower coefficient for the polymerization of olefins has been observed by Pease (17) and Geniesse and Reuter (9). The polymerization reactions play an important role in the complex reactions leading to the formation of aromatics, and perhaps determine chiefly the reaction rate.

EFFECT OF TIME FACTOR

Since variation in time or in temperature gave equivalent results in respect to yield of volatile oils over a rather wide temperature range, an intermediate temperature, 850° C., was selected for a series of experiments in which the time factor



alone was varied, and more complete data taken. The gas subjected to cracking was the same as that used for the preceding experiments. Sufficiently large quantities of gas were cracked to give several grams of liquid products in each experiment. Tar and volatile oils were collected and measured separately and the gases were analyzed. The data are shown in Table I.

COMPOSITION OF GASEOUS PRODUCTS. The sequence of changes taking place during the reaction is best shown by the change in the composition of the gases (Figure 3). The primary decomposition of the propane and butanes into

simpler paraffins and olefins was nearly complete in 0.0025 minute during which time oil formation was negligible. The time consumed by the succeeding oil-forming stage of the reaction was many times greater. During this stage methane formation increased to a high final value, hydrogen increased somewhat, and with the exception of ethylene and ethane the other gaseous hydrocarbons were quickly destroyed. Because of the relatively long time required by the oil-forming stage of the pyrolysis, certain reactions which have been observed in association with the more rapid primary decomposition of paraffins have an opportunity to play an important part. The reversible hydrogenation of ethylene to ethane maintains ethane in nearly equilibrium concentration when the gas composition is changing slowly, as experiments to be discussed will show. Work in progress indicates that the hydrogenation of olefins higher than ethylene, such as propylene and the butenes, results in the formation of products of primary decomposition of the corresponding paraffins; and, since breaking of the carbon chain takes place and methane is an important product, much of the methane is probably formed in this way without the intermediate formation of polymers. Ethylene and ethane survive because the two-carbon chain is not subject to breaking of the carbon-carbon bond.

LIQUID PRODUCTS. The effect of time of contact on the yield of liquid products is shown in Figure 4. During the early part of the oil-forming stage of the reaction, the yield of volatile liquid products increased rapidly, accompanied by a rather rapid decrease in gaseous olefins, then became constant during the period 0.03 to 0.08 minute while the olefins de-creased more slowly. The volatile oil was associated with very little tar during the early stages of its formation, but tar continued to increase after a maximum yield of volatile oils had formed, owing, no doubt, to the formation of tar from the latter. Carbon formation became marked at a still later stage and accelerated only when much tar had formed, due to its formation in turn by the degradation of tar. The volatile oils first formed contained unsaturated hydrocarbons, but the oil surviving the longest exposure time of 0.40 minute crystallized partly at 0° C. and consisted almost entirely of benzene. The effect of change in time on the composition of the volatile liquid products is shown in more detail in a later section.

TABLE I. CRACKING OF GAS MIXTURE⁴ AT 850° C. WITH

| | V AG LL | NG LIME | or Con | IACI | | |
|----------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------|------------------------------------------------|----------------------|------------------------------|------------------------------|-------------------------------------------------|
| Run | 1 | 2 | 3 | 4 | 5 | 6 |
| Time of contact, minutes | 0.0025 | 0.006 | 0.010 | 0.042 | 0.08 | 0.40 |
| gaseous prod- ucts to inlet gas | 1.8 | 1.8 | 1.9 | 2.1 | 1.8 | 2, 2 |
| Yields, weight %: Volatile oils Tar Carbon | $3.0 \\ 0.2 \\ 0.03$ | $\begin{array}{c} 8.1\\ 1.4\\ 0.13\end{array}$ | $9.4 \\ 1.9 \\ 0.10$ | $\substack{14.2\\9.5\\0.60}$ | $\substack{13.5\\12.5\\1.3}$ | $8.7 \\ 14.7 \\ 11.5$ |
| Analysis of gase- ous products, % by vol.: | | | | | | |
| $\begin{array}{c} \mathrm{CO}_2 \\ \mathrm{N}_2 \\ \mathrm{O}_2 \\ \mathrm{H}_2 \end{array}$ | 0.0^{h} 3.4 0.6 | $0.0b \\ 5.7 \\ 0.0 \\ 13.2 $ | No analysis | 0.0° 3.1 0.7 | 0.3° 7.6 1.4 | 0.0° 0.5 0.6 25.0 |
| CO CH4 | $ \begin{array}{c} 12.0 \\ 0.0 \\ 32.8 \end{array} $ | 0.3 41.3 | | 0.7 48.5 | $0.3 \\ 58.0$ | $\begin{array}{c} 20.0\\ 0.0\\ 63.5\end{array}$ |
| C₂H₄ C₂H₅ | $\substack{22.6\\5.2}$ | $26.6 \\ 3.3$ | | 5.8 | ò. | ò. |
| C_3H_6 C_3H_8 | $\substack{10.7\\7.2}$ | $3.8 \\ 4.7$ | | · · · · | •• | · · · · |
| C4H8 C4H10 | 1.5 1.8 | $\begin{array}{c} 0.9\\ 0.2 \end{array}$ | | | ••• | • • |
| Higher hydro- carbons Unsaturates | 1.9d | <i></i> | | 22.7 | 14.0 | 9.5 |
| Total | 100.0 | 100.0 | | 100.0 | 100.0 | 100.0 |
| ^a Composition of | f gas mixtu | re meth | ane 18.69 | nronan | 44 7 % | n-butane |

Composition of gas mixture: methane 18.6
 27.7%, isobutane 4.0%.
 b Fractionation analysis.
 c After removal of benzene (Orsat analysis).
 d Volatile oils present.

Portions of tar from runs 3, 5, and 6 were dissolved in five volumes of pyridine, and to the solution was added an equal volume of pentane. The tar from a 0.01-minute exposure gave no precipitate, but tar from the 0.08- and 0.40-minute exposures gave increasingly heavy brown precipitates, presumably of aromatic hydrocarbons of high molecular weight formed by protracted cracking.

CARBON. Some carbon was always obtained in the form of a hard lustrous coating. A flake of carbon, obtained from an experiment in which butane was cracked at 750° C. for a period of 2.3 minutes, was crushed and examined under the microscope. It was found to consist of spherical particles about 1 micron in diameter, cemented together. Similar spherical particles were obtained from tar formed by drastic cracking as a residue after repeated extraction with pyridine. The form of the carbon suggests that the particles were built up while suspended in the gas and were deposited subsequently on the walls of the tube.



850° C. ON COMPOSITION OF GAS

HEAT OF CRACKING REACTION. From the heat of formation of the reactants and products, the variation in heat content through the cracking period was calculated, assuming a constant temperature of 850° C. For the heats of formation of volatile oils and tar there were taken for convenience the values per unit weight for benzene and naphthalene, respectively (8). Figure 5 shows the calculated heat-content curve. About 650 calories per gram were required to heat the uncracked gas to reaction temperature, after which the rapid primary decomposition took place with absorption of heat followed by the slower oil-forming reactions with evolution of heat. The point of maximum heat content corresponds to the formation of a maximum concentration of gaseous olefins at an exposure time of about 0.0025 minute. The exothermic heat developed between 0.0025 and 0.08 minute was about 190 calories per gram, enough to raise the temperature about 200° C. In large-scale experiments to be described, a marked exothermic effect from this cause has been observed.

A large-scale experimental unit for cracking gas was constructed in which the endothermic and exothermic reaction stages were conducted separately under conditions suitable for each. The endothermic cracking took place in a tube coil of chromium-alloy steel. The charging stock was butane, which was cracked at 750° to 770° C. at 2 atmospheres pressure to a maximum content of unsaturates of 43 per cent by volume. The gas at 770° C. then passed into an insulated chamber in which the formation of aromatic hydrocarbons took place without any further introduction of heat and over a much longer period of time. The temperature rose 50° C. during the passage through the chamber. Under these conditions a maximum yield of benzene was obtained with a minimum time of contact. By reducing the flow rate of the gas and thus increasing the time of contact, the formation of a larger amount of tar took place with a corresponding increase in exothermic heat. Under such conditions a temperature rise in the chamber proper exceeding 100° C. was observed.

| TABLE II. | EXPERIM | ENTS 4 | ат Ехт | веме Те | MPERAT | URES |
|---------------------------------------|------------|------------|----------|--------------|-----------|---------|
| Run | 1 | 2 | 3 | 4 | 5 | 6 |
| Material treated | Butane | Butane | Butane | Propane | Propane | Propane |
| Temperature, ° C. Time of contact, | 600 | 600 | 600 | 1050 | 1050 | 1050 |
| minutes | 5 | 11 | 30 | 0.00015 | 0,0003 | 0.0005 |
| Yields, weight %: Volatile liquids | 3 | 13 | 13 | 11.5 | 14.0 | 13.0 |
| Density d ₄ ²⁵ | 0.815 | 0.830 | 0.850 | | • • | • • |
| Tar | 0 | (4) | (5) | 6.0 | 10.0 | 16.0 |
| Analysis of gase- ous products: | a | | | | | |
| N2 | 10.5 | 0.0 | 4.2 | | | |
| CO_2 | 0.0 | 0.4 | 0.0 | 0.6 | • • | |
| | ó ó | +.0 9 4 | 6.3 | 0.8 | | |
| ČH₄ | 30.0 | 24.0 | 55.9 | 35.8 | | |
| C_2H_4 C_2H_6 | 9.1 7.7 | 43.4 | 15.5 | ó.ó | • • | ••• |
| C_3H_6 | 14.8 | | | | | |
| C_3H_8 | 3.9 | | | | | |
| C.H. | 4.0 | | | | | |
| C_4H_{10} | 20.0 | | | | | |
| Unsaturated | | 25.0 | 16.9 | 28.9 | | |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | | |
| ^a Free from lig | uid hydroc | arbons; | analyses | calculated a | air-free. | |

EXPERIMENTS AT EXTREME TEMPERATURES. While the yield of oils and the general course of the cracking reactions are substantially the same within a wide temperature range, certain differences are to be expected at different temperatures. Table II shows the results of experiments in which butane (11 per cent isobutane) was cracked at 600° C., and propane was cracked at 1050° C., using several times of contact for each. The hydrogen concentration, in both the early and later stages of oil formation, was much higher at the high temperature than at the low one. This may be attributed to the increase in the dissociation of the paraffins (especially ethane) into olefin and hydrogen with increase in temperature. The volatile oils formed at 600° C. increased in density as the



time was prolonged, reaching 0.850 in 30 minutes, which is only a little lower than the density of benzene. This indicates that chiefly aromatics were formed even at this rather low temperature. The liquid hydrocarbons formed at 1050° C. (presumably aromatic) were not examined.

At 850° C. the primary decomposition was nearly complete before the formation of liquid hydrocarbons from the olefins so produced became appreciable (Table I). But since the temperature coefficient of rate is higher for the former reaction than the latter, it would be expected that at low temperatures the formation of oils would get under way before the primary decomposition was complete. In the experiments at 600° C. this effect is apparent. Table II, run 2, shows the formation of a nearly maximum yield of volatile oils, while much ethane and higher paraffins still survive. This is shown by the analysis of the gases produced. The paraffins were determined by combustion and calculated as methane and ethane. The low apparent value of methane is due to the presence of paraffins higher than ethane.

Effect of Pressure

The cracking of an ethane-propane fraction of natural-gas condensate under pressure to obtain aromatic hydrocarbons has been studied by Davidson (4). Two reaction stages were observed, but the interpretation was complicated by the fact that the pressure and time factors were not separated. It



appeared desirable to conduct experiments in which the time factor was varied independently. For this purpose, propane of 99 per cent purity was cracked at one pressure (9.5 atmospheres) and 750° C., using several times of contact. The method was the same as that used in the preceding experiments except for modifications made in the apparatus to permit the use of pressure. The cracking was conducted in a silica tube of 6 mm. inside diameter. The tube was fitted snugly into a chrome-steel tube, and the end was cemented to the steel tube to prevent the passage of gas over the steel surface. The propane was introduced under the cylinder pressure into the tube, and the products were withdrawn at the pressure of the system through a condenser and electrical precipitator kept at a temperature of 0° C. The clean gas issuing from the precipitator under pressure was discharged at the desired constant rate from a needle valve through a condenser immersed in an acetone-solid carbon dioxide bath, and stored. At the end of the run the volatile oil was distilled from the precipitator; and the gas, volatile oil, and tar were separated in the usual way. In calculating the time of contact, the pressure was taken into account. Table III shows the results of three experiments under pressure; one experiment (run 4) in which propane was cracked at atmospheric pressure and a higher temperature (850° C.) is included for comparison. In run 1 the time of contact was not quite long enough to complete the primary decomposition. The formation of liquid hydrocarbons did not become marked until the primary decomposition was nearly completed. Carbon appeared in significant amounts when a considerable amount of tar had formed. In these respects the results are analogous to those obtained at atmospheric pressure (Table I). Since the rate of polymerization is increased by pressure, it would be expected that the rate of oil formation would be increased in this case. Such an effect is not sufficiently marked to be shown by these few data. The yield of volatile oils was about the same as that obtained at atmospheric pressure. In the later stages of cracking, much ethylene was tied up in the form of ethane. This

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should decrease its rate of conversion into oils and allow any further yield increase to be offset by the conversion of volatile oils into tar.

TABLE III. CRACKING OF PROPANE UNDER PRESSURE

| Run | 1 | 2 | 3 | 4 | 5ª |
|------------------------------------------------------------------------|-----------------------------------------|-------------------------------------------------------------------------------|----------------------|----------------------|---------------------------------------------------------------|
| Temperature, ° C. Pressure, atmospheres Time of contact, minutes | $750 \\ 9.5 \\ 0.09$ | $750 \\ 9.5 \\ 0.22$ | $750 \\ 9.5 \\ 0.30$ | $850 \\ 1.0 \\ 0.04$ | $750 \\ 1.0 \\ 0.70$ |
| products to inlet gas | 1.45 | 1.9 | 1.8 | 2.0 | 0.95 |
| Yields, weight %: Volatile oils Tar Carbon | 3.5 | 13.5 | 16.0 11.0 1.4 | 15.5 8.0 | } 15 |
| Analysis of gaseous prod- ucts, % by vol., air- free: | | | | | |
| CO_2 | 0.0b | 0.20 | 0.00 | 0.80 | 120 |
| $ \begin{array}{c} $ | $0.6 \\ 25.8$ | $ \begin{array}{c} 0.9 \\ 1.7 \\ 66.2 \end{array} $ | 0.0 68.8 | $1.3 \\ 55.8$ | $12.9 \\ 1.7 \\ 56.7$ |
| $egin{array}{c} C_2H_4 \ C_2H_6 \end{array}$ | $\begin{array}{c}13.5\\11.3\end{array}$ | 13.6 | 14.3 | (0.3) | $\begin{smallmatrix}12.1\\3.7\end{smallmatrix}$ |
| C_3H_6 C_3H_8 | $11.1 \\ 28.0$ | | ••• | • • | $0.9 \\ 0.0$ |
| ${}^{{ m C_4H_8}}_{{ m C_4H_{10}}}$ | $\begin{array}{c} 0.6\\ 0.7\end{array}$ | | ••• | | 0.0 0.0 |
| Higher hydrocarbons Unsaturates | 1.7d | 11.4 | 9.0 | 19.0 | $ \begin{smallmatrix} 0.0 \\ (N_2) & 12.0 \end{smallmatrix} $ |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

^a Gas used was obtained from cracking of butane in a previous experiment. ⁶ Fraction analysis.
⁶ After removal of volatile oils; Orsat analysis.
⁴ Higher hydrocarbons includes volatile oils.

The gas analyses show, by comparison with similar experiments at atmospheric pressure and the same temperature, a much higher ratio of ethane to ethylene. The reaction

$$C_2H_6 \rightleftharpoons C_2H_4 + H_3$$

is driven to the left by increase in pressure; and, because of the comparative rapidity of the reaction, equilibrium is approached. Calculating from the data of Pease and Durgan (18) at 750° C.,

$$K \; \frac{(C_2H_4)(H_2)}{(C_2H_6)} \; = \; 0.45$$

concentrations being expressed in atmospheres. Assuming the unsaturates in the gas from run 3 to be only ethylene, K = 0.50. Ethane, ethylene, and hydrogen were present in nearly equilibrium proportions. For comparison an experiment (run 5) is included in Table III in which another gas, produced by the cracking of butane, was cracked again at the same temperature but at atmospheric pressure. The calculated value of K is 0.40, also in good agreement with the equilibrium value. Where satisfactory ethane determinations are available, the concentrations found are not far from equilibrium values, provided that the cracking has proceeded so far that the gas composition is changing slowly.

Composition of Volatile Oils

While the sequence of changes taking place during the cracking of simple paraffins to produce aromatic oils is affected little by temperature except in respect to velocity over a wide temperature range, temperature no doubt has an effect on the composition of oils formed at equivalent timetemperatures, especially at the lower temperatures and in the initial stages of their formation.

In order to obtain more detailed information about the composition of the volatile oil, several experiments with different flow rates were conducted at an intermediate temperature, 850° C. (Table IV), under the conditions of those reported in Table I, except that sufficient quantities of gas were treated to furnish liquid products for a complete analysis. For these experiments, butane containing 11 per cent isobutane was pyrolyzed.

ANALYSIS OF LIQUID HYDROCARBONS. The liquid hydro-carbons were condensed from the gas at -78° C. to insure the condensation of the low-boiling hydrocarbons above propane. The lower-boiling part of the tar was separated by distillation and added to the volatile oil which was then promptly subjected to a careful fractional distillation below 15° C. in a modified form of the column used for gas analysis. The distillate was collected in the following fractions: propylene, butenes, pentenes, hexenes, benzene, benzene-toluene intermediate fraction, toluene, toluene-xylene intermediate fraction, xylene-styrene fraction, and tar. The condensate obtained from run 2, for which the time of contact was short, contained a high proportion of unsaturates and for this reason was selected for an examination of the fractions as follows:

To the butene fraction cooled in an acetone-solid carbon dioxide bath was added dropwise a small excess of bromine. After standing overnight at room temperature, the excess bromine was removed and the bromides distilled at a pressure of 1 mm. of mercury to a final temperature of 90° C. The residue was identified as the tetrabromide of 1,3-but diene by separating 50 per cent of it as the higher-melting isomer, melting at 118° C. A separate portion of the butene fraction in the gaseous condition was passed into 65 per cent sulfuric acid in the Orsat apparatus, and found to consist chiefly of isobutene, which is absorbed more readily than butadiene or the normal butenes in acid of this concentration.

During the separation of the pentene fraction, a small proportion, assumed to be pentenes, was observed to boil around 36 and most of the remainder at a constant temperature of 42° C. Both cyclopentadiene and piperylene boil at 42° C. The fraction was shown to contain little but the former substance by keeping it at room temperature for several days to permit polymerization of any cyclopentadiene, which proceeds much more rapidly than in the case of the other pentadienes. The fraction was then distilled. The distilling temperature rose immediately to 170° C., the boiling point of the cyclopentadiene dimer. Little distillate was obtained at a lower temperature, which indicated that only small amounts of hydrocarbons other than cyclopentadiene were present. The identity of this component with cyclopentadiene was confirmed by condensing it with acetone in the presence of sodium ethoxide according to Thiele (21).

The hexene fraction was found by bromination to contain chiefly diolefins. A hydrocarbon was present which gave a condensation product with acetone. It was later separated in the pure state from a quantity of benzene and found to boil at 72.7° C. (760 mm.). This hydrocarbon is probably methylcyclopentadiene. It passes over into the dimer quite rapidly at room temperatures, but the rate is somewhat slower than that of cyclopentadiene.

The benzene fraction was found to melt at 4.5° C. It contained a small amount of unsaturates, estimated by bromine titration.

The toluene fraction also contained a very small amount of unsaturates. At a few degrees above the boiling point of toluene, a bright vellow hydrocarbon was obtained during the fractionation. The quantity was too small for identification.

The xylene fraction contained chiefly xylenes, but a large pro-portion of styrene was also present, as well as a small amount of another yellow hydrocarbon not identified.

The analyses for the several runs at different flow rates are shown in Table IV. In the early stages of benzene formation, butadiene, and cyclopentadiene, as well as less abundant higher unsaturates, are present in fairly large amount. With prolonging of the reaction time, the proportion of these diolefins decreases. They should be regarded as transient in character, the rate at which they are destroyed exceeding the rate of formation from gaseous olefins as the concentration of the latter decreases. The concentration of toluene also decreases somewhat with increased reaction time. Benzene, however, continues to increase up to the longest reaction time used. A comparison with the data of Table I indicates that a further increase in time would have decreased the yield of volatile oils. While significant amounts of unsaturates of 4 and 5 carbon atoms per molecule were formed, very little of the unsaturates were found in the boiling range of benzene

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and toluene. The tendency for larger hydrocarbon molecules other than aromatics to survive is evidently small. Nearly all the unsaturates occurring in benzene formed at this temperature were diolefins, and of these the cyclopentadienes were present in largest amount.

EFFECT OF RAW MATERIAL CRACKED ON BENZENE YIELD

Since all the lower normal paraffins except methane decompose into smaller paraffins and olefins in a time much shorter than that required for subsequent benzene formation, it is evident, as has been pointed out by Hague and Wheeler (10), that the optimum time-temperature conditions for benzene formation should be nearly the same for all. The lower olefins and other lower paraffins should also require the same conditions. A high yield of methane is invariably formed along with the aromatic hydrocarbons by reactions involving the consumption of hydrogen, and no other paraffins usually survive in significant amounts. Since the carbon required to form methane is unavailable for the formation of aromatic hydrocarbons, the yield of oils depends upon the carbon not consumed in this way, and the carbon-hydrogen ratio of hydrocarbon material to be converted into aromatic oils may be used as an index of the yield to be expected. Table V shows the results of experiments in which several different hydrocarbons were cracked under conditions giving a maximum weight per cent yield of volatile oils containing little but benzene and toluene. Ethane (runs 1 and 2) gave a distinctly lower yield than propane (run 3). Ethylene (run 4) gave a greater yield. The addition of hydrogen to propane caused a marked decrease (run 5). Kerosene (run 7) gave a slightly lower yield than would be expected from its hydrogencarbon ratio, but this should perhaps be expected in the case of high molecular-weight hydrocarbons which are not wholly converted into small molecules by the primary decomposition.

| TABLE IV. | Composition | OF | VOLATILE | Oils | FROM | BUTANE | AT |
|-----------|-------------|------|----------|------|------|--------|----|
| | | - 85 | 50°C. | | | | |

| Run | 1 | 2 | 3 | 4 | 5 |
|----------------------------------------------------|--------------------|------------------------|----------|---------------------|-------|
| Time of contact, minutes | 0.0015 | 0.015 | 0.04 | 0.065 | 0.15 |
| Vol. ratio exit gaseous prod- ucts to inlet gas | 2.0 | 1.9 | 2.1 | 2.3 | 2.4 |
| Yields, weight %: | - • • | | | | |
| Volatile oils | 3 | 10.5 | 15.5 | 16.0 | 17.0 |
| Tar Analyzia of gasseys mod | 0.0 | 5.0 | 9.0 | 11.0 | 17.0 |
| ucts. % by vol.: | | | | | |
| CO_2 | 0.0 | 0.0 | No | 0.7 | 0.1 |
| | 10.0 | 16.7 | analysis | 16.6 | 28.1 |
| ČH₄ | 23.1 | 148 4 | | 157 4 | 10.09 |
| C_2H_6 | $\frac{4.2}{25.5}$ | ∫ ± 0. ± | |) 07 . 1 | 100.0 |
| C2H4 C.H. | 16.0 | | | •• | |
| C_3H_5 | 0.0 | | | | |
| C ₄ H ₅ | 4.4 | | | | |
| C ₄ H _{1k} | 15.9 | 31.4 | | 02.0 | 11.3 |
| Olisaturates | | | | | |
| Total | 100.0 | 100.0 | | 100.0 | 100.0 |
| Analysis of volatile oils, | | | | | |
| Propylene | | 3 | 0.9 | 0.7 | ì |
| Butenes | | 5 | 35 | 3 | |
| Butadiene Pentenes | | 4 | }. | ~ • | §1.9 |
| Cyclopentadiene | | 6 | }4 | 2.5 | |
| Hexadienes | | 1 | 0.3 | 0.5 | 200.0 |
| Benzene | | 61.1 | 74.8 | $\frac{82.8}{1.0}$ | 92.0 |
| Toluene | | 9.85 | 12.0 | 9.5 | 5.8 |
| Intermediate | | 0.15 | 0.0 | 0.0 | 0.0 |
| Ayienes plus styrene | | | (2) | | · · · |
| Total | | 100.00 | 100.0 | 100.0 | 100.0 |

The properties of the tar varied with the material cracked. The tars produced by the cracking of ethane, and of propane plus hydrogen, were transparent, yellow-brown, and quite fluid. The tar from ethylene was almost black and quite viscous. This difference is probably due to a difference in concentration of hydrogen, a high hydrogen content favoring the formation of a light tar, perhaps by destroying certain components.

TABLE V. YIELD OF VOLATILE OILS FROM SEVERAL HYDRO-CABBONS

| Run | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|----------------------------------------------------|-------------|----------|---------------|--------------------------------------------|----------------------------------|---------------------------------------------|----------------|
| Material cracked | C_2H_6 | C_2H_6 | C_3H_3 | C_2H_4 | $C_{3}H_{*}$ + H ₂ | Kero- sene ^a | Kero- |
| Temperature, ° C. | 850 | 850 | 850 | 725 | 850 | 850 | 850 |
| Vol. ratio exit gaseous prod- | 0.05 | 0.10 | 0.04 | 1.0 | 0.05 | 0.02 | 0.05 |
| material | 1.5 | 1.5 | 2.0 | 0.92 | 1.5 | 4.8^{b} | 8.35 |
| Yields, weight %: Volatile oils Tar | 10.5 | 10.5 | $15.5 \\ 8.0$ | $\begin{array}{c} 23.5\\ 18.5 \end{array}$ | $9.5 \\ 6.0$ | $\begin{array}{c} 16.5 \\ 22.0 \end{array}$ | $19.0 \\ 32.0$ |
| Analysis of gase- ous products, ° % by yol.: | | | | | | | |
| <u>C</u> O ₂ (1 | N_2) 1.2 | 0.1 | 0.8 | 0.3 | 1.0d | 0.0 | 0.2 |
| H ₂ | 37.1 | 41.8 | 22.8 | 14.8 | 7.8 | 22.1 | 25.0 |
| CH4 | 22.8 | 34.9 | 55.8 | 33.8 | 57.6 | 48.0 | 55 3 |
| C_2H_6 | 6.9 | 4.8 | (0.3) | 20.7 | 3.6 | 2.2 | Õ |
| Unsaturates | 31.0 | 17.8 | 19.0 | 29.5 | 29.0 | 27.7 | 19.3 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| | | | | | | | |

^a From Midcontinent crude.
^b Ratio of gas volume to vapor volume.
^c Free from volatile oils.

d Calculated free from added hydrogen. The gas treated was a mixture of equal volumes of propane and hydrogen.

Conclusions

1. The cracking of the lower paraffins, with the exception of methane, to produce benzene and toluene may be conducted within the rather wide temperature range of 700° to 1050° C., provided that the correct time-temperature values are used.

2. The pyrolysis proceeds through a rapid endothermic decomposition in which simple olefins are formed, which is followed by a much slower exothermic reaction during which the olefins are converted into aromatic hydrocarbons.

3. In the neighborhood of 850° C., butadiene and cyclopentadiene are the chief low-boiling hydrocarbons formed, other than the benzene and toluene which predominate in the volatile oils.

4. The yield of benzene and toluene from the lower paraffins and olefins increases with the carbon-hydrogen ratio.

Acknowledgments

The authors are indebted to G. G. Oberfell and R. C. Alden for their generous support, and to J. A. Guyer for information obtained from large-scale experimentation.

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RECEIVED October 31, 1931. Presented as part of the Symposium on "The Utilization of Gaseous Hydrocarbons" before the Division of Petroleum Chemistry at the 82nd Meeting of the American Chemical Society, Buffalo, N. Y., August 31 to September 4. 1931.

Thermal Decomposition of Alunite

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LUNITE as a possible commercial raw material for chemical industry was brought into the field of active investigation in 1912 when Butler and Gale (2) published results of their investigation of the chemical and geological nature of the alunite deposits found near Marysvale, Utah. A report by Waggaman (12) in the same year discussed "Alunite as a Source of Potash" and showed that potassium sulfate could be leached from alunite which had been calcined at about 700° C. Following these reports, several patents were issued on methods of recovering potash and other compounds from alunite.

A process by Tilley (11) recovers the potash as potash alum by digesting the crushed ore with sulfuric acid at 90° C. for 24 to 48 hours. The undissolved ore residue is converted to aluminum sulfate by roasting, and is recovered as such. Moldenke (10) has proposed a similar treatment, except that calcination is carried out in steps in a circulating atmosphere of sulfur dioxide and oxygen.

Chappell (7) treats the alunite with sulfuric acid and, after precipitating the aluminum as hydrate with ammonium hydroxide, produces mixed sulfates of ammonium and potassium to be used for fertilizer. In other patents (5, 6)he recommends slow calcination at 750° to 1000° C. in a strong current of air, and calcination in two steps, first at 600° C. and finally at 900° to 1000° C., after which the hot material is dumped into water to leach out potassium sulfate.

The progressive stages of decomposition of Utah alunite, effected by heating the material at constant temperatures and over a temperature range from 100° to 850° C., have been observed through the medium of chemical analysis. Combined water is liberated at 460° C., and complete decomposition of the aluminum sulfate to form alumina results at 800° C. Potassium sulfate is not decomposed by heating at this temperature and has been leached from the calcined material and recovered as 99.26 per cent pure potassium sulfate. The residue after leaching consists mainly of aluminum oxide containing small amounts of silica, iron oxide, and magnesia.

Cameron and Cullen (4) obtain potassium alum by digestion of the ore with sulfuric acid at 110° C., and recover the product in a way similar to the process of Tilley.

Detwiller (9) prepares a nitric acid solution of the alumina and potassium while the silica remains insoluble. Soluble nitrates and sulfates are recovered.

Blough and McIntosh (1) sinter a mixture of finely ground alunite and sodium chloride at 800° C. and leach out soluble salts, after which the sodium sulfate and insoluble alumina are heated together at temperatures

less than 1500° C. to form soluble sodium aluminate.

Although the greater number of patents include decomposition of the ore by heating, no literature has been found to show either the rate or completeness of decomposition at given temperatures.

The work presented herewith was done to determine by means of chemical analyses the course of the thermal decomposition of Marysvale alunite.

CHEMICAL NATURE OF ALUNITE

Alunite is a naturally occurring, hydrated double sulfate of aluminum and potassium of the approximate composition represented by K₂O·3Al₂O₃·4SO₃·6H₂O. Impurities, such as silica and salts of iron, magnesium, and sodium, are usually present in small and varying amounts.

| | | TABLE I. | Analyses of Alunite from Various Sources | | | | | | |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|------------------------------------|------------------------------------------------------------------------------|--------------------------------|---------------------------|---------------------------------------------|--------------------------------------------|
| SOURCE | SiO1 % | Al2O3 % | so: % | K2O % | Na2O % | Fe1O1 % | MgO % | H₂Oª % | H2Ob % |
| Theoretical (8) Marysvale, Utah ^c Marysvale, Utah (2) Marysvale, Utah (2) Rico Mts., Colo. (2) Rito Mts., Colo. (2) Silverton, Colo. (2) Tres Cerritos, Calif. (2) | $\begin{array}{c} 0.95\\ 0.22\\ 5.28\\ 2.54\\ 1.79\\ 0.50\\ 2.64 \end{array}$ | $\begin{array}{c} 37.0\\ 38.38\\ 37.18\\ 34.30\\ 42.35\\ 37.66\\ 39.03\\ 38.05 \end{array}$ | $\begin{array}{c} 38.6\\ 35.52\\ 38.34\\ 36.54\\ 35.24\\ 35.24\\ 37.92\\ 38.93\\ 38.50\end{array}$ | 11.410.2110.469.713.276.774.264.48 | $\begin{array}{c} 0.56\\ 0.33\\ 0.56\\ 4.02\\ 2.12\\ 4.14\\ 2.78\end{array}$ | 0.13 Trace Trace 0.23 | 0.84 0.38 Trace | 0.14 0.09 0.11 0.13 0.06 Nil | 13.013.0212.9013.0811.9913.0313.35a+t11.92 |
| | ~ | | | | | | | | |

^G Water removed at 105° C.
^b Water of combination removed at 460° C.
^c Alunite used in this investigation.

Cameron (3) calcines the ore at 500° C., causing a restricted evolution of sulfur oxides. The soluble aluminum compounds are leached and alum separated. The latter is then calcined at 750° C., forming potassium sulfate and alumina, which is digested with hot water to yield a solution of the potash salt.

Table I shows the composition of representative samples of raw alunite from different localities and from different mines in the same locality.

The natural product is practically insoluble in water, but, after calcination at temperatures which produce partial decomposition of the original structure, potassium sulfate and