TWO MECHANISMS OF CARBON FORMATION
IN THE DECOMPOSITION OF n-PARAFFINS,
NAPHTHENES, AND AROMATIC HYDROCARBONS
WITH SIX AND SEVEN CARBON ATOMS
ON SILICA GEL

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The existence of differences in the pyrolysis of some hydrocarbons at comparatively low and high temperatures has been reported previously by a number of authors [1-3]. We showed [4, 5] that the difference in the pyrolysis of benzene homologs on silica gel at different temperatures is expressed most clearly in carbon formation. Two carbon-formation mechanisms (low-temperature up to 660-745° and high-temperature above 745-785°) are observed in the decomposition of benzene homologs; in the case of benzene itself, there is only one mechanism over the same temperature range.

The change in mechanism appears as a check in carbon formation in the temperature range 660-785° at 7-9% conversion of the original hydrocarbon into carbon and as a new increase in carbon-formation rate with a further rise in temperature. The low-temperature mechanism may be represented as a multistage dehydrocondensation with a complete use of the carbon of the starting materials, while the high-temperature mechanism is dehydrocondensation of benzene nuclei with preliminary dealkylation of starting alkylbenzenes. With the low-temperature mechanism, the condensation proceeds mainly through the alkyl groups; with the high-temperature mechanism, it proceeds through the nuclei. The change in mechanism is caused by the development of destructive hydrogenation of the starting hydrocarbons or their dehydrocondensation products by the hydrogen liberated in carbon formation. In the present investigation we attempted to determine whether there is a difference in the carbon-formation mechanism at different temperatures in the decomposition of other hydrocarbons, in particular, cyclohexane, methylcyclohexane, n-hexane, and n-heptane in comparison with benzene and toluene.

EXPERIMENTAL

The experiments were carried out by the same procedure as in the previous investigation [5], i.e., in a quartz reactor of a flow, heterogeneous catalytic apparatus with an indirect-temperature regulation system [4, 6, 7], over the temperature range 500-900° at atmospheric pressure. The same silica gel of KSM grade with a grain size of 1-2 mm was used as a catalyst. A fresh portion (5 ml) of catalyst was used for each experiment. The reagents (Table 1) were introduced at the same rate of 4.78 ml/hr. Each experiment lasted for 2 hr. The apparatus was flushed with nitrogen before and after an experiment. The carbon was determined with an accuracy of up to 0.0001 g by direct weighing; the tarry condensation products were determined by analysis of the quantitatively-collected catalyzate with an accuracy of 1% of the value determined. The gaseous products were determined by means of a Patrikeev automatic gasometer (UGSP) and subjected to analysis on a BTI apparatus and low-temperature rectification on a TsIATIM-51u apparatus. The liquid part of the catalyzate was distilled on a fractionating column with an efficiency of 30 theoretical plates and the substances obtained were identified.
TABLE 1

Constants of Starting Hydrocarbons

<table>
<thead>
<tr>
<th>Starting hydrocarbon</th>
<th>B.p. in °C (p in mm Hg)</th>
<th>$d^2_4$</th>
<th>$n^2_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>79.1 (743)</td>
<td>0.8790</td>
<td>1.5013</td>
</tr>
<tr>
<td>Toluene</td>
<td>109.2 (748)</td>
<td>0.8669</td>
<td>1.4965</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>78.6—78.8 (750)</td>
<td>0.7811</td>
<td>1.4272</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
<td>99.2—100.4 (761)</td>
<td>0.7685</td>
<td>1.4234</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>68.1—68.5 (750)</td>
<td>0.6599</td>
<td>1.3751</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>96.0—98.0 (744)</td>
<td>0.6838</td>
<td>1.3879</td>
</tr>
</tbody>
</table>

The characteristics of benzene and toluene decomposition on silica gel will not be discussed here as special attention was devoted to them in our previous communication [5]. In the present discussion, we will present only data on the behavior of these hydrocarbons which is necessary for comparison with the naphthenes and paraffins investigated in this work.

Fig. 1. Temperature dependence of carbon formation (conversion of hydrocarbon introduced into carbon in %) during the decomposition of benzene (1), cyclohexane (2), n-hexane (3), toluene (4), methylcyclohexane (5), and n-heptane (6) on silica gel.

As Fig. 1 shows, the increase in the rate of carbon formation with a rise in temperature in the case of cyclohexane, methylcyclohexane, n-hexane, and n-heptane shows a check in the temperature range 690—825° which is specific for each of the hydrocarbons. The check in carbon formation is analogous to the phenomenon for toluene and lies in approximately the same temperature range as for toluene and other benzene homologs. Evidently, the reason for the given check in carbon formation in the case of the naphthenes and paraffins investigated is also a change in the carbon-formation mechanism, as in the case of alkylbenzenes.