TWO MECHANISMS OF CARBONIZATION IN THE DECOMPOSITION OF BENZENE HOMOLOGS ON SILICA GEL

A.P. Rudenko, A.A. Balandin, and I.I. Grashchenko

M.V. Lomonosov Moscow State University
Translated from Izvestiya Akademii Nauk SSSR. Otdelenie Khimicheskikh Nauk, No. 4, pp. 605-613, April, 1960
Original article submitted September 15, 1958

At the present time, investigators are becoming increasingly convinced that carbonization under cracking and pyrolysis conditions is polycondensation of starting materials or some of their preliminary conversion products adsorbed on the catalyst [1-8]. Moreover, the opinion that the carbonaceous material formed during the pyrolysis of organic substances is elementary ("pure") carbon, which was introduced by Berthelot [9] and maintained by a number of investigators [10-12], is gradually being replaced by the idea of the carbonaceous material as the product from polycondensation of benzene nuclei or other intermediate compounds [13-20]. In the general case, carbonization is the polycondensation of some starting material and in each actual case there is a specific mechanism, which is determined by the nature of the starting material. This is either dehydrocondensation of benzene [3], butadiene polymerization [2], polycondensation of acetaldehyde [8], or some such process. If there is a change in the starting material for carbonization with a change in the pyrolysis conditions, then there must be a change in the mechanism of this process. One of us observed such a phenomenon previously [3] in the form of two different carbonization mechanisms in the pyrolysis of toluene, o-xylene, and mesitylene, one of which occurred at comparatively low temperatures and the other at high temperatures. Together with this, it was reported that there is only one carbonization mechanism in the pyrolysis of benzene over the same temperature range (500-900°). The present work is a more detailed investigation of this phenomenon on a large number of examples.

EXPERIMENTAL

The experiments were carried out with an automatic flow apparatus for heterogeneous catalytic investigations with an indirect temperature-regulation system [21], which made it easy to select the required temperature and maintain it with an accuracy of ±0.2° at 800°. The apparatus had a demountable quartz reactor, which made it possible to remove and weight the catalyst and the carbonaceous material formed on it without dismantling the apparatus [3, 22]. The experiments were carried out at 500-900° and atmospheric pressure. The catalyst was 5 ml of KSM grade silica gel, ground to 1-2 mm and purified. A fresh portion of catalyst was used for each experiment. The reacting material (Table 1) was introduced at a rate of 4.78 ml/hr. The duration of each experiment was 2 hr. The apparatus was flushed with nitrogen before and after an experiment. The carbonaceous material was assayed by direct weighing with an accuracy of 0.0001 g and the volatile dehydrocondensation products were determined by analysis of the quantitatively collected catalyze with an accuracy of 1% of the value determined. In addition, the gaseous products were analyzed on a VTI apparatus and the catalyzates distilled on a fractionating column with an efficiency of 30 theoretical plates. The substances isolated by distillation were identified by the boiling points, refractive indices, and qualitative reactions. The procedure was described in more detail in [3].
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_20^0</th>
<th>n_20^0</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>m-Xylene</td>
<td>135.7—136.2 (749)</td>
<td>0.8649</td>
<td>1.4989</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>140.5—141.0 (745)</td>
<td>0.8824</td>
<td>1.5038</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>135.5—136.0 (746)</td>
<td>0.8601</td>
<td>1.4964</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>135.5—136.5 (757)</td>
<td>0.8652</td>
<td>1.4960</td>
</tr>
<tr>
<td>Mesitylene</td>
<td>160.5—161.0 (749)</td>
<td>0.8623</td>
<td>1.4996</td>
</tr>
<tr>
<td>Cumene</td>
<td>148.7—149.0 (741)</td>
<td>0.8636</td>
<td>1.4918</td>
</tr>
</tbody>
</table>

TABLE 2

Results of Analyses of Catalysis Gases

<table>
<thead>
<tr>
<th>Starting hydrocarbon</th>
<th>Experiment temperature in °C</th>
<th>Composition of catalysis gases in vol. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>hydrogen</td>
</tr>
<tr>
<td>Benzene</td>
<td>842</td>
<td>100</td>
</tr>
<tr>
<td>Toluene</td>
<td>636</td>
<td>100</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>690</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>786</td>
<td>49</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>690</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>787</td>
<td>33</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>660</td>
<td>~100</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>638</td>
<td>100</td>
</tr>
<tr>
<td>Mesitylene</td>
<td>716</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>784</td>
<td>43</td>
</tr>
<tr>
<td>Cumene</td>
<td>660</td>
<td>~100</td>
</tr>
<tr>
<td></td>
<td>722</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>799</td>
<td>85</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>639</td>
<td>90</td>
</tr>
<tr>
<td>Mesitylene</td>
<td>717</td>
<td>51</td>
</tr>
<tr>
<td>Cumene</td>
<td>845</td>
<td>70</td>
</tr>
</tbody>
</table>

DISCUSSION OF EXPERIMENTAL RESULTS

As Fig. 1 shows, the carbonization rate during the pyrolysis of benzene increased steadily with a rise in temperature, while in the case of toluene, m-xylene, and mesitylene, its increase with a rise in temperature suffered a check in a temperature region which was specific for each of these hydrocarbons and at approximately 7-9% conversion of the starting hydrocarbon to carbonaceous material. The beginning of the check in the increase in carbonization rate for toluene was at 745°, for m-xylene, 695°, and for mesitylene, 660°. If we compare the results of analyses of the catalysis gases (Table 2) and distillation of the catalytes (Table 3) for experiments at temperatures below and above the "beginning of the check" indicated here, it can be seen that before the beginning of the check in carbonization, methane was practically absent from the catalysis gases and a lower boiling fraction than the original hydrocarbon was practically absent from the catalytes, while at higher temperatures in the gases there appeared large amounts of methane and in the catalytes, lower boiling hydrocarbons. The check in the increase in the carbonization rate for benzene homologs was evidently connected with successive demethylation of the hydrocarbons and the formation of lower homologs and finally benzene.