MECHANISM OF CARBON FORMATION IN THE DECOMPOSITION OF METHANE, ETHANE, ETHYLENE AND ACETYLENE ON SILICA GEL

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It was shown earlier [1] from the results of our preceding investigations that the number of possible mechanisms of carbon formation for the decomposition of an organic compound is determined by the number of carbon forming materials of different chemical types which may be both the original materials and the products obtained from their earlier conversion. The change from one mechanism of carbon formation into another is realized when the variation in the conditions is such that one carbon forming material disappears and another appears or where the process of carbon formation from one carbon forming material is inhibited and is dependent on the other. Each mechanism of carbon formation which we studied earlier, represented the process of polycondensation of carbon forming material resulting in the formation of more and more complex polycyclic macromolecules — carboids composing the carbon substance. In the pyrolysis of methane we observed one carbon formation mechanism [1]. In this case, since a certain quantity of ethane, ethylene and acetylene was obtained as well as carbonaceous substance and hydrogen it was of interest to study the process of carbon formation in the decomposition of these hydrocarbons, as well as methane, under comparable conditions and to determine the importance of each of them as a carbon forming material.

EXPERIMENTAL

The procedure used in the work was the same as that described earlier [1, 2]. The experiments were carried out at atmospheric pressure in a catalytic apparatus, in a flow system, the apparatus containing a detachable quartz reactor. Silica gel (KSM), particle diameter 1-2 mm, used as the charge, was placed in the reactor. In each test 5 ml of fresh silica gel was taken. The carbonaceous material obtained was directly calculated by weighing the reactor with an accuracy of 0.0001 g. The tarry products were collected and quantitatively determined with an accuracy of about 1% of the amount being determined. The rate of evolution of the gaseous products was determined with the aid of a Patrikeev recording gas meter. In each experiment the contact gases were completely analyzed by means of a chromatographic method, the volumes of the separated components being read visually. The feed velocity of the original hydrogen was about 0.06 mol/hr which was controlled by a flow gauge. The composition of the original hydrocarbons are given in the table. Methane and acetylene were drawn from cylinders of the gases. Ethane and ethylene were synthesized: ethane, by the electrolysis of a solution of sodium acetate with subsequent purification of the gas in the appropriate absorbents and by means of low temperature fractionation; ethylene by the dehydration of ethyl alcohol over aluminum oxide at 400°C followed by purification.

<table>
<thead>
<tr>
<th>Original hydrocarbons</th>
<th>Components</th>
<th>Hydrogen</th>
<th>Methane</th>
<th>Ethylene</th>
<th>Acetylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>0</td>
<td>96.3</td>
<td>1</td>
<td>0</td>
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<td>Ethane</td>
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<td>0</td>
<td>99.4</td>
<td>0</td>
<td></td>
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<tr>
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<td>0</td>
<td>1.2</td>
<td>98.2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Acetylene</td>
<td>0</td>
<td>0</td>
<td>traces</td>
<td>99.5</td>
<td></td>
</tr>
</tbody>
</table>

High Temperature Mechanisms of Carbon Formation

It follows from Fig. 1, that the rate of carbon formation in the decomposition of methane increases smoothly with a rise in temperature and in the same way, the yields of the tarry products increase. The composition of the contact gases also gradually alter (Fig. 2A). These properties are evidence of the existence of only one mechanism of carbon formation in the decomposition of methane as was shown in the earlier investigation [1].

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In the case of ethane, ethylene and acetylene, on the contrary, the rates of carbon formation undergo abrupt changes in temperature regions specific for each of these hydrocarbons (cf. Fig. 1A); the yields of the tarry products also pass through maxima at temperature regions specific for each hydrocarbon (Fig. 1B); and the gas composition undergoes sudden intermittent changes in the curves with increase of temperature (Fig. 2B, C, D). In support of this conclusion analogous observations have been reported earlier with a change in the mechanism of carbon formation with the decomposition of alkyl benzenes, naphthenes, higher paraffins and alcohols on catalysts [1-4]. Thus, in the case of ethane, ethylene and acetylene it is possible to take note of two mechanisms of carbon formation: low and high temperature transformation where a change occurs in the following temperature ranges: 875-910°, 810-850°, 620-750° correspondingly.

It should be noted that the maximum formation of tar in the case of ethane, ethylene and acetylene, depending on the temperature range, coincides with the upper limits of these given range for the change in the mechanism of carbon formation (cf. Fig. 1A and 1B) i.e., after passing through the maxima the rates of tar formation begin to decrease suddenly with increase of temperature with a parallel abrupt increase of the rates of high temperature carbon formation. The latter condition may be explained by the fact that aromatic hydrocarbons* which are present in the tarry products are the carbon forming materials in the high temperature mechanism. However, in practice, the complete coincidence of the carbon formation curve for the high temperature mechanism in the case of ethane with the carbon formation curve for methanol (cf. Fig. 1A) and the small yields of tarry products in comparison with the carbonaceous substances makes us think that the tarry products are not the only carbon forming materials in the high temperature mechanism of carbon formation. Comparison of the composition of the contact gases obtained by the decomposition of ethane and methane in the temperature range of the high temperature mechanism (above 910°) shows how close they are, both by quantitative ratio of the components and by the direction of the change in gas composition with temperature (cf. Fig. 2A and 2B). This in its turn is evidence that the carbon forming material and the mechanism of carbon formation in this temperature region for ethane and methane used as the initial hydrocarbons, are the same. Consequently, in the case of the high temperature mechanism of carbon formation from ethane, the previously produced aromatic tar and methane are the carbon forming materials, whereas with an increase in temperature, the proportion of the tar as the carbon forming material decreases but the proportion of methane increases. Thus, on the basis of comparing the rates of carbon formation from ethane and methane (cf. Fig. 1A) the proportion of tar as carbon forming material may be approximately estimated as 50% at 950° and 0% at 975°.

In the case of high temperature carbon formation from ethylene and acetylene, methane is also obviously a carbon forming material along with the aromatic tars which is proved by the diminishing proportion of methane in the hydrocarbon part of the contact gases (cf. Fig. 2C and 2D). However, comparison of the rates of carbon formation from these hydrocarbons and from methane in the region of the high temperature mechanism (cf. Fig. 1A) shows

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* The tarry products give very pronounced qualitative reactions for aromatics with concentrated sulphuric acid; they give a green fluorescence in benzene solutions—a property of condensed aromatics; the major constituents in certain cases is naphthalene separated from the tar by crystallization and identified by its melting point in the pure form and by the mixed melting point. The presence of different condensed aromatic hydrocarbons: naphthalene, diphenyl, phenanthrene, anthracene etc., in the tarry products from the pyrolysis of the compounds which we investigated, has been reported earlier in numerous investigations [5-11 and others].