CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

COMMUNICATION 17. PARTICIPATION OF 2-BUTENE IN THE HYDROCONDENSATION REACTION WITH CARBON MONOXIDE

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We have previously reported results on the hydrocondensation of carbon monoxide with 1-butene [1] and 2-butene [2] under identical conditions: temperature 190°, pressure atmospheric, carbon monoxide concentration 4-6% on the original gas mixture of 70-75% butene and 20-25% hydrogen, space velocity about 100 hour⁻¹. Comparison of the hydrocondensation products of 1-butene and 2-butene*, of the physical constants of fractions having an identical boiling range, and of the Raman spectra of these fractions shows that these products do not differ qualitatively and consist essentially of hydrocarbons of normal structure: there is an admixture of only a very small amount of branched hydrocarbons having one methyl side group. This result was very unexpected for reaction with 2-butene, since normal hydrocarbons can be formed by hydrocondensation only from 1-butene: as in this process the reaction center in the olefin molecule is the double bond, 2-butene should give only branched hydrocarbons. The mild conditions of the reaction practically exclude the possibility of skeletal isomerization. Hence, if unchanged 2-butene were to undergo the hydrocondensation reaction at any appreciable rate, it would be expected that appreciable amounts of branched hydrocarbons would be found among the reaction products, which is not observed experimentally. The same could be said of the products of the hydrocondensation of 1-butene, for it has been shown previously [3] that 1-butene is readily isomerized to 2-butene under the conditions of the reaction.

Our results give reason to suppose that, in the hydrocondensation of 1- or 2-butene, the products are always formed from 1-butene, into which 2-butene must first be isomerized. On this basis we should expect that no difference would be observed between 1- and 2-butenes in the hydrocondensation reaction. However, when the results on the hydrocondensation of carbon monoxide with 1-butene [1] and with 2-butene [2] are compared, not only resemblances, but also substantial differences can be observed.

The identical extents to which hydrogen participates in the overall process should be noted: in both cases it reacts to the extent of 54-55%, calculated on the original amount of hydrogen. There is little difference also in the extents to which carbon monoxide takes part: 52.2% in the case of 1-butene and 45.6% in the case of 2-butene. The same may be said of the hydrocracking products, which amount to not more than 3-4% of the 1- or 2-butene that undergoes reaction. Among the differences that should be noted we must first of all refer to the considerable difference in the value of the total yield of liquid hydrocarbons: 730-975 ml/cu.m, or 70-100 ml/liter-hour, for the reaction of 1-butene and 350-540 ml/cu.m, or 35-55 ml/liter-hour, for the reaction of 2-butene (ratio about 2). Correspondingly, the degree of conversion of 1-butene is 74%, and that of 2-butene is 47%. There is a difference also in the content of unsaturated hydrocarbons in the hydrocondensate (52% and 37%); moreover, the average molecular weight of these is greater in the case of 2-butene, as can be seen from the relative amounts of heavy and light oils and the sizes of the individual fractions. In the hydrogenated hydrocondensate the C₅ fractions amount to 8% and 0.8% respectively, the C₆ fractions to 8.6% and 6.1%, and the C₇ fractions to 9.7% and 8.4%. The yield of butane, which characterizes the hydrogenation of the butenes, is 9.4% for 1-butene and 5.0% for 2-butene (on the amount of original olefin that reacted). This increased yield of butane and greater total yield of hydrocarbons in the reaction with 1-butene must explain the equal extent to which hydrogen takes part in the two cases.

At first glance it may appear that all those features of the 2-butene reaction which we have described as

* See Table 3 and Fig. 2 in our Communications 15 [1] and 16 [2].
substantially different from those of the 1-butene reaction must contradict the view that the hydrocondensation products from 2-butene are formed essentially from 1-butene, into which 2-butene is first isomerized. However, on a closer examination it is found that these differences not only do not contradict this view, but, on the contrary, find their explanation in this general scheme of reaction and confirm the hypothesis that the rate of the reaction of 1-butene in hydrocondensation with carbon monoxide is very much greater than the rate for 2-butene, the direct reaction of which is extremely slow:

\[ \nu \text{C}_4\text{H}_8 - 1 \gg \nu \text{C}_4\text{H}_8 - 2; \nu \text{C}_4\text{H}_8 - 2 \rightarrow 0, \]  

and that the hydrocondensation reaction of 2-butene proceeds essentially via the intermediate formation of 1-butene.

Let us examine the relative amounts of the reactants on the catalyst surface in the two cases. In the reaction with 1-butene, the catalyst contains adsorbed hydrogen, carbon monoxide, 1-butene, and a fairly large amount of 2-butene, which is formed from 1-butene and will not exceed the latter in amount. We have shown previously [3] that, under the same reaction conditions but in absence of carbon monoxide, the relative amounts of 1- and 2-butenes in the gas phase of the reaction product is 1:1.1 when the original hydrocarbon is 1-butene (in presence of hydrogen). It was found also [1] that, when carbon monoxide is added, the amount of 1-butene that isomerizes to 2-butene is 16% on the amount of olefin that reacts. Hence, for the butene concentrations at the catalyst surface in experiments on the hydrocondensation of carbon monoxide with 1-butene we may write:

\[ [\text{C}_4\text{H}_8 - 1]' \geq [\text{C}_4\text{H}_8 - 2]' \]  

When the original hydrocarbon is 2-butene, hydrogen and carbon monoxide are adsorbed on the catalyst surface in about the same amounts as in the experiments with 1-butene; 2-butene and small amounts of 1-butene formed from 2-butene are also adsorbed. The fact that the 1-butene concentration is indeed low in this case is clear from the results of our previous investigations [1, 3], in which no 1-butene could be detected in the gas phase after experiments with mixtures of 2-butene, hydrogen, and carbon monoxide or of 2-butene and hydrogen. The explanation is that, when the volume of the original 2-butene is comparatively small, the 1-butene formed from it in small amount remains adsorbed on the catalyst surface; in presence of carbon monoxide it enters the hydrocondensation reaction, being continually regenerated by isomerization from 2-butene.

Hence, for the butene concentrations at the catalyst surface in experiments on the hydrocondensation of carbon monoxide with 2-butene we may write:

\[ [\text{C}_4\text{H}_8 - 2]' \gg [\text{C}_4\text{H}_8 - 1]' \]  

However, it is clear from experiments on the isomerization of 1- and 2-butenes [3] that

\[ [\text{C}_4\text{H}_8 - 2]' \geq [\text{C}_4\text{H}_8 - 2]' \]  

and from (3) and (4) it follows that

\[ [\text{C}_4\text{H}_8 - 2]' \gg [\text{C}_4\text{H}_8 - 1]' \]  

and from (2) and (5) we have

\[ [\text{C}_4\text{H}_8 - 1]' \gg [\text{C}_4\text{H}_8 - 1]' \]  

On the basis of the above considerations it follows that

\[ \frac{[\text{H}]}{[\text{C}_4\text{H}_8 - 1]}' \gg \frac{[\text{H}]}{[\text{C}_4\text{H}_8 - 1]}' \]  

and

\[ \frac{[\text{CO}]}{[\text{C}_4\text{H}_8 - 1]}' \gg \frac{[\text{CO}]}{[\text{C}_4\text{H}_8 - 1]}' \]