Reports of the Academy of Sciences of the USSR

N. I. ERSHOV, Ya. T. EIDUS, and V. R. EROKHINA

1960

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1960. Vol. 133, No. 1

CHEMISTRY

N. I. ERSHOV, Ya. T. EIDUS, and V. R. EROKHINA

OXYGEN-INITIATED HETEROGENEOUS-CATALYTIC POLYMERIZATION OF ETHYLENE IN THE PRESENCE OF HYDROGEN

(Presented by Academician B. A. Kazanskii, March 10, 1960)

We have established that the reaction of ethylene hydrogenation at atmospheric pressure and a temperature of 100° in the presence of a Co–clay contact (a catalyst for the hydropolymerization of olefins under the action of carbon monoxide ([1])) is accompanied by a polymerization reaction with formation of a gaseous dimer and liquid hydrocarbons. This observation is unexpected, since until now, in the hydrogenation of ethylene over the same contact, but at a somewhat higher temperature of 190–200°, ethylene polymerization was not observed unless the initial gas contained carbon monoxide, even in negligible amounts ([2]). A more detailed investigation showed that the polymerization of ethylene in the presence of hydrogen at 100° is initiated not by carbon monoxide, but by oxygen present as a small impurity in the initial gas mixture. In contrast to the reaction of ethylene hydropolymerization under the action of small amounts of carbon monoxide, which proceeds more intensively as the temperature is raised in the range 120–200°, the reaction initiated by oxygen, on the contrary, weakens as the temperature is raised in this range and proceeds most intensively at 100–120°. The reaction is enhanced by increasing the concentration of oxygen in the initial gas mixture within the range studied, up to 2%, and does not proceed in the absence of oxygen. The reaction also does not proceed with ethylene alone in the absence of hydrogen. In the present work, some results are briefly set forth from a study of this new type of heterogeneous-catalytic polymerization of ethylene in the presence of hydrogen, initiated by small amounts of oxygen.

The apparatus, composition and method of preparation of the catalyst, and the procedure for carrying out the experiments remained as before ([1,2]). Each portion of catalyst (18 g) contained 5 g of metallic cobalt. The volume of catalyst in the reaction tube (made of Pyrex glass, 10 mm in diameter) was 25 ml. The experiments were carried out in a flow system at a space velocity of the initial gas mixture of about 100 hr^{-1}. Ethylene was obtained either by

dehydration of ethyl alcohol over alumina, or, when it was necessary to exclude carbon monoxide completely from the initial mixture, from ethylene bromide in an alcoholic medium with zinc dust ([3]). Electrolytic hydrogen was used in the experiments. The ethylene and hydrogen from which the initial gas mixtures were prepared were freed practically completely from oxygen (less than 0.1% O_2) by separate passage over reduced copper at 170°. The reaction products were trapped in two receivers, the first at room temperature and the second at −80°. The exit gas was collected in a gasometer.

Table 1 gives the results of experiments carried out at 100° on different portions of catalyst with ethylene–hydrogen mixtures in which the volume ratio C_2H_4 : H_2 was varied in the range 1–3.2, and the oxygen content was 1–1.6%. It is seen from Table 1 that at 100° simultaneous

but polymerization occurs along with hydrogenation of ethylene to ethane, with formation of a gaseous dimer and liquid products amounting to 35% of the initial ethylene. Experiments were then carried out under the same conditions at 100° with ethylene alone containing 0.5–1.8% oxygen. It turned out that, in the absence of hydrogen, ethylene polymerization does not proceed. It should be noted that the exit gas obtained in the polymerization of ethylene at 100° usually contains 1–1.5% CO. It could therefore be assumed that this reaction

Table 1

Contact portion	Experiment no.	Duration of experiment, h	In the initial gas: C_2H_4 : H_2	In the initial gas: O_2 content, %	Yield based on initial ethylene, %: liquid hydrocarbons	Yield based on initial ethylene, %: butylene and butane	Yield of ethane based on initial hydrogen, %
1	1	3.5	3.0	1.0	traces	20.3	75.2
1	2	5	2.7	1.0	6.2	12.3	58.6
1	3	5	3.2	1.0	11.0	6.8	72.0
1	4	10	3.2	1.4	18.6	8.0	62.7
1	5	15	3.1	1.0	11.5	1.4	48.1
2	6	5	2.7	1.2	7.1	19.0	67.5
3	7	5	2.0	1.6	24.7	12.0	78.0
3	8	5	2.2	1.6	20.9	1.1	37.8
4	9	5	1.1	1.5	16.6	9.7	71.5

is identical with the reaction of ethylene hydropolymerization under the action

of carbon monoxide ([2]). In view of the fact that hydropolymerization under the action of carbon monoxide gives maximum yields of reaction products at 190-200° and is intensified as the carbon monoxide concentration is increased, it could be expected that polymerization of ethylene in the presence of hydrogen would likewise proceed more intensively as the temperature was raised to 190-200°, and upon addition of CO at 100°. In the experiments, however, the opposite was observed. Table 2 gives the results of experiments carried out at different temperatures on one and the same portion of catalyst and with one and the same mixture having the volume ratio C_2H_4 : H_2 = 1.1 and an O_2 content of 2%.

Table 2

Experiment no.	Duration of experiment, h	Reaction temperature, °C	Yield based on initial ethylene, %: liquid hydrocarbons	Yield based on initial ethylene, %: butylene and butane	Yield of ethane based on initial hydrogen, %
10	6	100	23.7	11.5	45.3
11	15	120	17.4	10.9	56.3
12	10	140	16.3	5.9	66.7
13	10	160	9.4	5.2	72.6
14	15	180	8.2	3.7	78.8
15	10	200	5.4	2.6	82.7
16	10	220	3.0	2.1	79.2

From the data of Table 2 it is seen that, as the reaction temperature is raised from 100 to 220°, the yield of ethylene polymerization products in the presence of hydrogen continuously decreases from 35% at 100° to 5% of the initial ethylene at 220°, while the yield of ethane simultaneously increases correspondingly from 45 to 79% of the initial hydrogen. Table 3 gives the results of experiments at different temperatures, showing the influence of addition of carbon monoxide on the course of polymerization and hydrogenation. It turned out that addition of 4.4% CO to

Table 3

Fig. 1. Dependence of the yield of polymerization products at 100° on the oxygen concentration in the initial gas mixture

Figure 1: Fig. 1. Dependence of the yield of polymerization products at 100° on the oxygen concentration in the initial gas mixture

Experiment no.	Duration of experiment, h	Reaction temperature, °C	In the initial gas: CO content, %	In the initial gas: O_2 content, %	In the initial gas: C_2H_4 : H_2	Yield of polymerization products based on initial ethylene, %	Yield of ethane based on initial hydrogen, %
17	12	100	4.4	1.2	2.4	0.0	5.9
18	8	120	4.4	1.2	2.4	1.6	9.7
19	12	150	4.4	1.2	2.4	10.4	38.5
20	12	190	4.4	1.2	2.4	32.9	53.5
21	12	190	–	1.2	3.5	5.6	61.2
22*	12	100	–	1.2	3.1	22.2	67.1

* Before this experiment the catalyst was regenerated with hydrogen at 450° for 3 h.

The CO–H_2 mixture with a volume ratio C_2H_4 : H_2 = 2.4 and an O_2 content of 1.2% suppresses polymerization and causes a sharp retardation of hydrogenation at 100° (experiment 17). Noticeable formation of polymerization products begins at 120° and increases with increasing temperature. At the same time, hydrogenation of ethylene to ethane also intensifies. At 190° the yield of polymerization products reaches 33% of the initial ethylene, and the ethane yield 53.5% of the initial hydrogen (experiment 20). In the absence of carbon monoxide the ratios are the opposite: at 100° the yields of polymerization products and ethane are, respectively, 22 and 67% (experiment 22), i.e., both reactions proceed intensely, whereas at 190° (experiment 21) hydrogenation proceeds with the same intensity and the ethane yield is 61%, while polymerization practically does not occur (the polymerizate yield of 5.6% should be ascribed to the action of traces of CO remaining in the reaction system from the preceding experiments). Thus, the reaction of ethylene polymerization in the presence of hydrogen at 100° is not identical with the reaction of hydropolymerization of ethylene under the action of carbon monoxide.

Fig. 1. Dependence of the yield of polymerization products at 100° on the

oxygen concentration in the initial gas mixture

The presence of CO in the exit gas, and also of hydrogen peroxide (detected by the reaction with titanic acid[4]) in the reaction water of some experiments, indicates that the oxygen present as an impurity in the initial gas mixture actively enters, during the reaction, into interaction with the principal initial components. It could be supposed that, in this process, surface active forms are produced which cause the onset of ethylene polymerization; in other words, oxygen may manifest itself as an initiator of the reaction. Obviously, if this supposition is correct, a change in the oxygen concentration should affect the course of the reaction, and exclusion of oxygen from the composition of the initial mixture should lead to the complete absence of polymerization products. This was also confirmed experimentally. As is seen from Fig. 1, in experiments carried out at 100°, with increasing oxygen concentration in the investigated range, the yield of polymerization products increases continuously. In experiments carried out with ethylene–hydrogen mixtures in which the oxygen concentration was less than 0.1%, no polymerization was observed.

All the foregoing shows that the ethylene polymerization reaction in the presence of hydrogen, first observed by us, which accompanies the hydrogenation of ethylene at 100° on a cobalt contact, is initiated by oxygen.

N. D. Zelinsky Institute of Organic Chemistry
Academy of Sciences of the USSR

Received
8 III 1960

REFERENCES

1. B. A. Kazanskii, Ya. T. Eidus, K. V. Puzitskii, N. I. Ershov, *Investigation of the catalytic polymerization and hydropolymerization of ethylene and its hydrogenation with carbon monoxide*, Publishing House of the Academy of Sciences of the USSR, 1955, p. 63.

2. Ya. T. Eidus, N. D. Zelinsky, N. I. Ershov, DAN, 60, 599 (1948).

3. A. Sabaneev, ZhRKhO, 9, 33 (1877).

4. L. Schönn, Zs. anal. Chem., 9, 41, 300 (1870).

Note: Figure translations are in progress. See original paper for figures.