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![Figure 1 chromatograms](figure)

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Figure 1: Figure 1 chromatograms

Abstract

Full Text

Physical Chemistry

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On the Question of the Possibility of Carrying Out Catalytic Dehydrogenation in a Chromatographic Regime

Recently, the possibility has emerged of carrying out chemical reactions in a separating "chromatographic" regime, in which the components of the reaction mixture and the impurities contained in it move through the reactor in the form of individual zones (⁀1-5). With sufficiently rapid establishment of equilibrium at the phase boundary (gas—solid, gas—liquid, etc.), the rate of movement of each component of the mixture is determined by the magnitude of the sorption coefficient. When reactions are carried out under conditions of such self-separation, a number of complications typical of ordinary statics and dynamics disappear; in particular, it becomes possible to shift the thermodynamic equilibrium, lower the reaction temperature, remove poisoning by products, etc. In one of the previous works (⁀1), results were presented on the study, in this regime, of the catalytic dehydrogenation of cyclohexane. It was of interest to investigate the possibilities of catalytic dehydrogenation, in a chromatographic regime, of *n*-butylenes to divinyl.

Fig. 1. Chromatograms recorded upon successive injections into the reactor of a mixture of *n*-butylenes. *I* —divinyl, *II* —β-cis-butylene, *III* —β-trans-butylene, *IV* —α-butylene. Temperature 250°, volumetric flow rate of the carrier gas $\omega = 75$ cm^3/min

The reaction was carried out on an ordinary alumina–chromia catalyst. The composition of the initial mixture of α- and β-butylenes was determined chromatographically. In some experiments, chromatographically isolated individual α-, β-cis-, and β-trans-butylenes were used.

To study the dehydrogenation of *n*-butylenes to divinyl, a gas-chromatographic method was employed. The experimental apparatus and the working procedure did not differ in principle from those described earlier (⁀1).

Figure 2

Figure 2: Figure 2

With successive introduction of samples onto the catalyst, the character of the chromatograms obtained gradually changes (Fig. 1). After introduction of the first pulse, chromatographic peaks are not observed at all, i.e., pure helium comes out of the column. With the following pulses, at first only a single peak of pure divinyl appears; its amount in subsequent pulses decreases, gradually reaching a limiting value; at the same time, along with divinyl, isomers of β-butylene and α-butylene appear.

Figure 2 presents the dependence of the yield of divinyl, based on reacted n-butene, on temperature, recorded at carrier-gas flow rates of 17 cm^3/min and 87 cm^3/min. As the temperature is raised, the yield increases. The curve for lower flow rates lies higher. The same figure also gives the calculated curve of equilibrium divinyl yields (6–8) for a dilution by a factor of 100. Since the dehydrogenation of butylenes to divinyl proceeds with an increase in volume, lowering the total pressure of the system leads to an increase in the equilibrium yields. Therefore it is very important to estimate correctly the degree of dilution by carrier gas of the butylenes introduced pulsewise into the reactor (since dilution is equivalent to lowering the pressure in the system). The dilution in the pulse was calculated approximately from the width of the peak of the outlet curve obtained after introducing a sample of n-butene into the catalytic reactor. Approximate calculations showed that the dilution does not exceed the abovementioned value of 100. Therefore the results obtained are naturally explained by the specific features of the reaction in the pulse chromatographic regime. The same conclusion is supported by experiments on dehydrogenation under dynamic conditions. With a hundredfold dilution of n-butenes with helium, even at 250°, the reaction products could not be detected chromatographically. In the pulse regime, however, dehydrogenation of n-butylene becomes noticeable at 100°, and when the volume of the injected dose is reduced to 0.3 cm^3, the formation of divinyl is already noticeable at 80–85°.

Fig. 2. Dependence of the divinyl yield on temperature at different flow rates. 1—ω_1 = 17 cm^3/min; 2—ω_2 = 87 cm^3/min. The dashed curve represents the equilibrium yields of divinyl for a hundredfold dilution, $p = 0.01$ ata.

Figure 3 gives the results of studying the dependence of the contents of the components in the reaction mixture on temperature for a space velocity $\omega = 17$ cm^3/min. From Fig. 3 it is evident that the quasi-stationary yield of divinyl increases continuously (after 7–10 pulses) with temperature.

A similar picture is also observed for flow rates of 42, 47, 55, 75, and 87 cm^3/min. At all the indicated flow rates there are optimum temperatures at which the content of β-trans- and β-cis-butylenes is maximal, while the maximum for β-trans-butylene is shifted toward higher temperatures. The divinyl content increases

Figure 3

Figure 3: Figure 3

Fig. 4

Figure 4: Fig. 4

up to 300°; in some experiments at 350° and above, a certain decrease in the divinyl content is observed. Apparently, along with dehydrogenation there occur reactions of double-bond migration and cis-trans isomerization, as is indicated by our experiments in which individual chromatographically isolated α-, β-cis-, and β-trans-butylenes were introduced into the reactor. In all cases the entire range of products was formed—α-, β-cis-, β-trans-butylenes and divinyl.

Fig. 3. Dependence of the gas-phase composition on temperature.
1—divinyl; 2—cis-butylene; 3—β-trans-butylene; 4—α-butylene.

The effect of the size of the introduced sample on the degree of conversion of *n*-butylene to divinyl was also studied. The experiments were carried out at a temperature of 300° and a volumetric rate of 55 cm^3/min. The data obtained are presented in Fig. 4. It is seen from the figure that, as the introduced sample is increased (from 0.3 cm^3 to 2.5 cm^3), the percentage conversion decreases. At the same time, the absolute yield of divinyl is practically independent (dashed curve in Fig. 4) of the size of the introduced sample. Apparently, a zero order of reaction is involved; however, more detailed kinetic studies will make it possible to answer this question unambiguously.

In studying the reaction of dehydrogenation of *n*-butylenes to divinyl on an alumina-chromia catalyst under dynamic conditions ([9]), it was also shown that the kinetic order of the reaction is close to zero. In the present work, the heats of adsorption ([4]) of *n*-butylene and divinyl on the alumina-chromia catalyst were also determined by the chromatographic method. The heat of adsorption of *n*-butene proved to be 2.40 kcal/mole, and that of divinyl 3.0 kcal/mole.

Fig. 4. Dependence of the degree of conversion of *n*-butylene on the size of the introduced sample. The dashed curve is the absolute yield of divinyl. Temperature 300°, $\omega = 55$ cm^3/min.

In attempts to determine the onset temperature of catalytic dehydrogenation, we discovered an interesting phenomenon, consisting in the fact that the width of the chromatographic peaks of butylene and divinyl, recorded immediately after the catalytic reactor (carrier-gas flow rate, $\omega = 17$ cm^3/min), initially increases with increasing temperature and then decreases. Apparently, in this case it is possible chromatographically to record the course of activated adsorption of butylene and divinyl on the catalyst. The maximum peak width (65°) corresponds to the conditions of the strongest chemisorption. A further increase in temperature (to 85-100°) leads to a sharp decrease in peak width, and in this temperature region the appearance of reaction products is observed. Both in the case of butylene and in the case of divinyl, a distinct temperature maximum is noticeable.

The catalytic dehydrogenation of *n*-butylenes to divinyl in a pulse chromatographic regime on an alumina-chromia catalyst has been studied. The yield of divinyl in carrying out dehydrogenation in the pulse regime at low temperatures (85-200°) exceeds the equilibrium values by 1.5-2 orders of magnitude. The heats of adsorption of butylenes and divinyl on the alumina-chromia catalyst were measured chromatographically. The possibility of measuring activated adsorption by the chromatographic method has been demonstrated.

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