Academician **I. N. Nazarov**, L. N. Ivanova, and B. A. Rudenko

![Fig. 1. Calibration curve of the instrument](figure)

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Abstract

Full Text

CHEMISTRY

Academician **I. N. Nazarov**, L. N. Ivanova, and B. A. Rudenko

DEHYDRATION OF UNSYMMETRICAL METHYLISOPROPYLETHYLENE AND ITS MIXTURES WITH TETRAMETHYLETHYLENE

In continuation of our studies on the dehydrogenation of tetramethylethylene and tert-butylethylene (^{1}), we investigated the dehydrogenation of unsymmetrical methylisopropylethylene, as well as its mixtures with tetramethylethylene, over industrial catalysts used for the dehydrogenation of butylene to divinyl. The starting hydrocarbons were obtained by dehydration of pinacolyl alcohol (^{2}), and from the resulting mixture of unsymmetrical methylisopropylethylene with tetramethylethylene (boiling range 55–74°, n_D^{20} 1.4082, d_4^{20} 0.706), unsymmetrical methylisopropylethylene (b.p. 55.8°/760 mm, n_D^{20} 1.3915, d_4^{20} 0.6825) and tetramethylethylene (b.p. 73°/760 mm, n_D^{20} 1.4122, d_4^{20} 0.708) were isolated by rectification. The dehydrogenation experiments were carried out in an apparatus of the flow-through type (^{1}); before the experiment, the catalyst was activated with hydrogen for 1 hour at 630°. Regeneration of the catalyst was carried out by passing a steam–air mixture at 630°. During regeneration of the K-16 catalyst, an increase in temperature of 30–59° was observed. The dehydrogenation of unsymmetrical methylisopropylethylene was conducted over catalysts K-12, K-16, and K-18 at a temperature of 630°, a space velocity of about 1500 l per liter of catalyst per hour, and with an eightfold dilution with steam. Usually 5 ml of catalyst was taken; the duration of the experiment was 1 hour.

Fig. 1. Calibration curve of the instrument

When the condensate was distilled, a fraction with b.p. 32–72° was collected; the content of diene hydrocarbons in it was determined by condensation with maleic anhydride (^{3}). By this method, in the condensates of all experiments on the dehydrogenation of unsymmetrical methylisopropylethylene, isoprene was identified from its adduct with maleic anhydride (^{4}) (m.p. 64°), and 2,3-dimethylbutadiene-1,3 from its adduct with maleic anhydride (^{5}) with m.p. 76°

and tetrabromide (6) with m.p. 138.5–139°. By distillation on a column of the condensate from experiments on the dehydrogenation of this hydrocarbon over catalyst K-16, isoprene and 2,3-dimethylbutadiene-1,3 were isolated in a ratio of 1 : 2. Distillation of the condensates obtained in the dehydrogenation of unsymmetrical methylisopropylethylene over K-18, as well as analysis of this condensate by gas-liquid chromatography, showed an isoprene : 2,3-dimethylbutadiene-1,3 ratio equal to 1.4 : 1.

Analysis of the condensate by gas-liquid chromatography was carried out on a column 5 mm in diameter and 2 m long, packed with kieselguhr (particle diameter 0.5–0.25 mm) wetted with dibutyl phthalate (14 g of dibutyl phthalate was taken per 30 g of kieselguhr). The working temperature of the column was

Table 1

Catalyst	Experiment No.	Hydrocarbon charged, g	Fraction collected with b.p. 35–72°, g	Content of diene hydrocarbons, %	Amount of diene hydrocarbons, g	Yield of diene hydrocarbons, % based on hydrocarbon taken
Dehydrogenation of unsymmetrical methylisopropylethylene						
K-16	X	27.60	21.70	16.35	3.55	12.85
K-16	XII	28.00	21.10	16.50	3.48	12.45
K-12	I	26.90	16.75	17.7	2.96	11.45
K-12	II	27.90	19.16	16.8	3.22	11.53
K-18	VI	30.7	12.60	23.9	3.15	10.25
K-18	VII	30.7	13.83	24.7	3.42	10.80

Catalyst	Experiment No.	Hydrocarbon charged, g	Fraction collected with b.p. 35-72°, g	Content of diene hydrocarbons, %	Amount of diene hydrocarbons, g	Yield of diene hydrocarbons, % based on hydrocarbon taken
Dehydrogenation of a mixture of 30% unsymmetrical methylisopropylethylene and 70% tetramethylethylene						
K-16	III	31.8	23.46	17.7	4.15	13.05
K-16	IV	31.8	23.51	16.6	3.93	12.30
K-12	I	29.0	19.9	23.3	4.63	15.95
K-12	II	29.2	18.79	23.1	4.34	14.95
K-18	IV	31.9	23.08	22.7	5.24	16.80
K-18	V	31.9	21.58	21.9	4.74	15.20

100°. Hydrogen was used as the carrier gas (10–15 ml/min). For analysis of the gas leaving the column, a modified microflame detector was used (7, 8).

The instrument was first calibrated on artificially prepared mixtures (Fig. 1).

Fig. 2. Analysis of the condensate by gas-liquid chromatography. *a* – condensate, experiment VI; *b* –artificial mixture containing, in addition to trimethylethylene and unsymmetrical methylisopropylethylene, 15% isoprene and 10% 2,3-dimethylbutadiene-1,3; *c* –the same mixture with tetramethylethylene added. Peak No. 1 corresponds to trimethylethylene, No. 2 to isoprene, No. 3 to unsymmetrical methylisopropylethylene, No. 4 to the unidentified product of isomerization reaction, presumably 2- or 3-methylpentene, No. 5 to tetramethylethylene, No. 6 to 2,3-dimethylbutadiene-1,3.

Fig. 3 and Fig. 4

Figure 2: Fig. 3 and Fig. 4

Comparison of the curve obtained in the gas-liquid chromatographic analysis of the condensate from experiment VI (see Table 1) with the curves corresponding to analysis of artificially prepared mixtures (Fig. 2) shows that the condensate contains, in addition to isoprene, 2,3-dimethylbutadiene-1,3 and the starting

hydrocarbon, also trimethylethylene and uninvestigated isomerization products, probably 2- and 3-methylpentenes. From a comparison of the chromatographic curves it is evident that the condensate does not contain tetramethylethylene —the possible isomerization product of unsymmetrical methylisopropylethylene. An attempt to isolate it in the form of the dibromide by treating the condensate with Br_2 in chloroform likewise was unsuccessful. The ratio of the peak heights of isoprene and 2,3-dimethylbutadiene-1,3 on the curve corresponding to the analysis of the condensate from experiment VI (Fig. 2, curve *a*, peaks Nos. 2 and 6) is equal to 2.5, which corresponds to their ratio in the condensate, 1.5 : 1 (Fig. 1).

The sum of diene hydrocarbons, determined by gas-liquid chromatography, is 23.0%, which is in good agreement with the data obtained by condensation with maleic anhydride (see Table 1). Table 1 presents the results of experiments on the dehydrogenation of unsymmetrical methylisopropylethylene.

Fig. 3. Effect of the composition of the initial hydrocarbon mixture on the dehydrogenation process.
1 —content of diene hydrocarbons in the condensate (wt. %); 2 —yield of diene hydrocarbons based on the mixture charged (%).

Fig. 4. Activity of the catalyst during many hours of operation without regeneration.

From the data in Table 1 it is evident that, under the conditions studied, this hydrocarbon on all three catalysts gives a steady yield of diene hydrocarbons (isoprene and 2,3-dimethylbutadiene-1,3) of the order of 10-13% based on the hydrocarbon charged.

Under analogous conditions, on catalysts K-12, K-16, and K-18, the dehydrogenation of a mixture of unsymmetrical methylisopropylethylene (30%) with tetramethylethylene (70%) was investigated. The results obtained are presented in Table 1.

The effect of the composition of the hydrocarbon mixture on the total yield of diene was studied on catalyst K-16. The behavior of mixtures containing unsymmetrical methylisopropylethylene at 10% (n_D^{20} 1.4118; d_4^{20} 0.7032), 30% (n_D^{20} 1.4012, d_4^{20} 0.706), 50% (n_D^{20} 1.4040, d_4^{20} 0.6925), and 75% (n_D^{20} 1.3975, d_4^{20} 0.683) was studied. The results obtained are presented in Fig. 3.

It is seen that increasing the content of unsymmetrical methylisopropylethylene to 30% causes a sharp decrease both in the total yield of diene hydrocarbons and in the percentage content of diene hydrocarbons in the condensate. Further dilution of tetramethylethylene with unsymmetrical methylisopropylethylene has a smaller effect.

The K-16 catalyst was tested under conditions of many-hour operation in the dehydrogenation of tetramethylethylene without regeneration after each experiment. It was shown (Fig. 4) that already after the first one-hour experiment the percentage content of diene in the condensate and the yield of 2,3-dimethylbutadiene-1,3 based on the hydrocarbon taken decrease sharply, remaining relatively constant thereafter. These data show that regeneration of the catalyst with a steam–air mixture should be carried out after the completion of each one-hour experiment. After regeneration, a catalyst that has operated continuously for 12 hours does not regain its initial activity (see Fig. 4).

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

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