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Abstract

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Interaction of 3-Methylpentene-2 with Cationic-Type Catalysts

Earlier investigations have been carried out ([1,2]), establishing the isomerizing action of cationic-type catalysts on the polymer chain of natural rubber. It was also shown that, simultaneously, other processes occur that are associated with the opening of double bonds in the isoprene unit, in particular cyclization processes ([1,3,4]). The present work is devoted to the study of these processes using 3-methylpentene-2, which models the structure of the polyisoprene unit, as an example. Ethylaluminum dichloride and titanium tetrachloride were used as catalysts.

Table 1

Composition of artificial mixtures of 3-methylpentenes-2 according to gas-chromatographic data

	Taken for analysis, %	Taken for analysis, %	Determined, %	Determined, %
	cis-isomer	trans-isomer	cis-isomer	trans-isomer
Mixture I	20.6	79.4	20.2	79.8
Mixture I	20.6	79.4	20.4	79.6
Mixture I	20.6	79.4	21.4	78.6
Mixture II	69.1	30.9	69.2	30.8
Mixture II	69.1	30.9	71.0	29.0
Mixture II	69.1	30.9	70.6	29.4

The starting hydrocarbon was synthesized by the method described ([5]) and isolated by rectification on a column. In the work, a fraction was used that contained 85.6% of the cis-isomer and 14.4% of the trans-isomer of 3-methylpentene-2, as well as a fraction boiling at 70.5°, representing the pure trans-isomer.

Table 2

Kinetics of the interaction of 3-methylpentene-2 with $Al(C_2H_5)Cl_2$ and $TiCl_4$. (Catalyst concentration 3.6 mole %, temperature 60°)

Catalyst	Duration of interaction, min.	Isolated, % of theory monomer	Isolated, % of theory dimer (by difference)	Monomer composition, % cis-	Monomer composition, % trans-
AlC_2H_5Cl	–	100	0	85.6	14.4
AlC_2H_5Cl	10	71.5	28.5	65.6	34.4
AlC_2H_5Cl	43	62.8	37.2	56.7	43.3
AlC_2H_5Cl	60	54.0	46.0	52.2	47.8
AlC_2H_5Cl	180	48.0	52.0	43.8	56.2
$TiCl_4$	8.0	79.0	21.0	82.7	17.3
$TiCl_4$	25	60.0	40.0	70.0	30.0
$TiCl_4$	35	55.2	44.8	66.3	33.7
$TiCl_4$	60	46.0	54.0	56.5	43.5
$TiCl_4$	90	40.0	60.0	48.5	51.5
Composition of the equilibrium mixture at 60°	–	–	–	42.2	57.8

The interaction between 3-methylpent-2-ene and the catalyst was carried out in an atmosphere of dry argon, without solvent. The 3-methylpent-2-ene contained 0.002 wt.% moisture, which, as is known, is a cocatalyst of cationic processes. After completion of the reaction, the mixture was treated with an aqueous KOH solution, washed with water to neutral reaction, and distilled. A fraction with b.p. 69.5–70.5°, representing a mixture of isomeric 3-methylpent-2-enes, and a second fraction with b.p. 188–193.5°, corresponding to the dimer of 3-methylpent-2-ene, were obtained.

The composition of the initial and isomerized methylpentenes was determined by gas chromatography on a laboratory chromatograph with a thermal-conductivity detector. Separation was carried out at 10° on a column of length 3 m and internal diameter 4 mm, packed with diatomaceous brick, particle size 0.5–0.25 mm, impregnated with dimethyl sulfoxide (25 parts by weight per 100 parts by weight of brick). Helium was used as the carrier gas, passed at a rate of 2.5 liters/hour. The higher-boiling isomer, which on passing through the chromatographic column is characterized by a longer retention time, is, according to the IR spectrum, the trans isomer.

Fig. 1. IR spectrum of the initial cis-3-methylpent-2-ene (1), and the same isomerized with $AlC_2H_5Cl_2$, in the region of 1300 cm^{-1} (2)

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Fig. 2. IR spectrum of the initial trans-3-methylpent-2-ene (1), and the same isomerized with $AlC_2H_5Cl_2$, in the region of 1300 cm^{-1} (2)

Fig. 2. IR spectrum of the initial trans-3-methylpent-2-ene (1), and the same isomerized with $AlC_2H_5Cl_2$, in the region of 1300 cm^{-1} (2)

The cis–trans isomer ratio was also determined using infrared spectra recorded on a UR-10 spectrograph in the region ···

750 cm^{-1}. Qualitatively, the presence of isomeric forms of 3-methylpentene was also observed in the region of 1300 cm^{-1}. The results of chromatographic analysis of artificial mixtures of cis- and trans-3-methylpentenes-2 on the chromatographic column used are given in Table 1.

Table 2 gives the results obtained in the interaction of 3-methylpentene-2, enriched in the cis form, with aluminum ethyldichloride and titanium tetrachloride.

As follows from the data of Table 1, under these conditions the process of cis-trans isomerization of 3-methylpentene-2 proceeds until equilibrium is established. The composition of the equilibrium mixture calculated by us coincides with that determined experimentally by other authors ([6]).

Figure 1 shows the IR spectra of 3-methylpentenes-2 in the region of 1300 cm^{-1}. The spectrum of the starting product has an isolated band at 1303 cm^{-1}, due to deformation (= CH) vibrations of the group $-C(CH_3) = CH-$ in the cis position.

As a result of isomerization, a band at 1320 cm^{-1} appears in the spectrum, which can be assigned to deformation (= CH) vibrations of the group $-C(CH_3) = CH-$ in the trans position (Fig. 1).

When cationic-type catalysts interact with the trans form of 3-methylpentene-2, an isomerization process is also observed, which can be seen qualitatively in Fig. 2, where the spectrum of isomerized trans-3-methylpentene-2 is presented. In the spectrum an intense band at 1303 cm^{-1} appears and, correspondingly, the band at 1320 cm^{-1} decreases (Fig. 2).

The process of isomerization of 3-methylpentene-2 is accompanied by the formation of dimeric products, the yield of which was determined from the difference between the weighed sample taken and the amount of methylpentene distilled off.

A special experiment during distillation of the high-boiling fraction showed that the entire product boils in the temperature interval 188–193.5° and contains no high-boiling impurities corresponding to trimer and other higher-molecular compounds. Analysis of the dimer was carried out by high-resolution NMR using an INM-3 spectrometer at a frequency of 40 MHz. Figure 3 shows the spectrum obtained for the dimer. The chemical shifts were determined relative to tetramethylsilane ([7]). The spectrum contains bands corresponding to the

resonance of protons located at an unsaturated carbon atom (5.0 τ), in methylene (8.05 τ) and methyl (8.40 and 8.50 τ) groups attached to an unsaturated carbon atom, as well as protons of methyl and methylene groups located at a saturated carbon atom (9.0 τ) (Fig. 3).

Fig. 3. High-resolution NMR spectrum of the dimer of 3-methylpentene-2

Fig. 3. High-resolution NMR spectrum of the dimer of 3-methylpentene-2.

The mechanism of interaction of cation-type catalysts with 3-methylpentene-2 can presumably be represented as follows:

$$\underset{\text{cis-isomer}}{H_3C{-}HC{=}C(CH_3){-}CH_2{-}CH_3} + H^+ \longrightarrow \tag{1}$$

$$\left[H_3C{-}H_2C{-}\overset{+}{C}(CH_3){-}CH_2{-}CH_3\right] \tag{2}$$

$$\left[H_3C{-}H_2C{-}\overset{+}{C}(CH_3){-}CH_2{-}CH_3\right] \xrightarrow{-H^+} \underset{\text{trans-isomer}}{H_3C{-}HC{=}C(CH_3){-}CH_2{-}CH_3} \tag{3}$$

$$\left[H_3C{-}H_2C{-}\overset{+}{C}(CH_3){-}CH_2{-}CH_3\right] + H_3C{-}HC{=}C(CH_3){-}CH_2{-}CH_3 \longrightarrow$$

$$H_3C{-}CH_2{-}C(CH_3){-}CH_2{-}CH_3 \quad H_3C{-}CH{-}\overset{+}{C}(CH_3){-}CH_2{-}CH_3 \tag{4}$$

$$\xrightarrow{-H^+} \text{dimers}$$

At stage (4), three directions of deprotonation are possible, involving the protons of carbon atoms adjacent to the cation. In this case tetra-, tri-, and disubstituted olefins may be formed. The NMR data show that tetrasubstituted olefins predominate in the mixture of dimers.

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