CHEMISTRY

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1960

SovietRxiv

Abstract

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ISOMERIZATION OF CERTAIN HEXENES IN THE PRESENCE OF ALUMINUM OXIDE

At the present time many reactions are known that are catalyzed by substances of acidic or basic character, whose action is based on acid–base interaction between the catalysts and the substances undergoing catalysis ([1]). Such reactions include, for example, the reaction of migration of multiple bonds in olefinic hydrocarbons, catalyzed both by substances of acidic character ([2]) (mineral acids, salts of strong acids and weak bases, aluminum oxide, etc.) and by substances possessing the properties of bases ([3]) (amides of alkali and alkaline-earth metals).

According to current concepts of the mechanism of these reactions, isomerization under the influence of acidic catalysts proceeds with the formation of intermediate carbonium ions ([4],[5]):

$$\cdot\mathrm{CH_2{=}CH{-}CH_2{-}CH_2{-}R} \xrightarrow{\mathrm{HA}} [\mathrm{CH_3{-}\overset{+}{C}H{-}CH_2{-}CH_2{-}R}]\,\mathrm{A^-},$$

whereas isomerization under the influence of alkaline metal amides proceeds with the formation of intermediate carbanions ([3])

$$\cdot\mathrm{CH_2{=}CH{-}CH_2{-}CH_2{-}R} \xrightarrow{\mathrm{MeNH_2}} [\mathrm{CH_2{=}CH{-}\overset{-}{C}H{-}CH_2{-}R}]\,\mathrm{\overset{+}{NH_3}Me}.$$

The same olefins, in the presence of catalysts of different character, may behave differently.

The influence of the structure of monoolefins on the ease of their isomerization in the presence of an alkaline catalyst—calcium amide—was investigated by us earlier, and it was established that, other conditions being equal, the rate of isomerization depends on the degree of substitution of the hydrogen atoms in the allylic position ([3]). In the present work the influence of the structure of monoolefins on the relative rates of migration of the double bond in the presence of an acidic catalyst—aluminum oxide—was studied.

Isomerization was carried out at 80° with a feed space velocity of 2.64 hr^{-1}, and, for hexenes that isomerize with difficulty, also at a velocity of 0.23 hr^{-1}. The relative rates of isomerization were characterized by the magnitude of conversion of the olefin under the same conditions.

Table 1

No.	Initial hexene	Space velocity, hr^{-1}	Isomerization, %	Equilibrium concentration of isomerization products at 80°, %
1	2-Methylpentene-1	2.6	62	84
2	2,3-Dimethylbutene-1	2.6	49	77
3	Hexene-1	2.6	0	98
3	Same	0.23	20	98
4	3-Methylpentene-1	2.6	0	99.5
4	Same	0.23	12	99.5
5	4-Methylpentene-1	2.6	0	99.5
5	Same	0.23	4	99.5

The results of the experiments are given in Table 1. For comparison, we give the values calculated by us for the equilibrium state: the total concentrations of isomerization products differing from the initial hexene in the position of the double bond.

The data of Table 1 clearly indicate the difference in the behavior of the hexenes: the first two isomerize rapidly, while the last three, on the contrary, do so very slowly.

The easy isomerizability of 2-methylpentene-1 and 2,3-dimethylbutene-1 is explained by the presence at the double bond of methyl groups, which have an electron-donor character and facilitate addition of a proton to the olefin with formation of a carbonium ion. The remaining three hexenes, which have no alkyl substituents at the double bond, form a carbonium ion with more difficulty and, consequently, isomerize more slowly.

The results obtained make it possible to select correctly the isomerization catalyst and the conditions for carrying out an experiment for an olefin of a given structure or, conversely, to avoid the undesirable isomerizing action of substances with acidic properties in the course of any other reactions (hydrogenation, alkylation, etc.).

Experimental Part

Characteristics of the initial hexenes. Hexene-1: b.p. 63.20; n_D^{20} 1.3880; d_4^{20} 0.6731. 2-Methylpentene-1: b.p. 62.2; n_D^{20} 1.3922; d_4^{20} 0.6803. 3-Methylpentene-1: b.p. 54.2; n_D^{20} 1.3848; d_4^{20} 0.6673. 4-Methylpentene-1: b.p. 53.8; n_D^{20} 1.3830; d_4^{20} 0.6641. 2,3-Dimethylbutene-1: b.p. 55.7; n_D^{20} 1.3907; d_4^{20} 0.6778.

Procedure for carrying out the experiments. Isomerization was carried out in a flow system at 80° with space velocities of 2.64 hr^{-1} and 0.23 hr^{-1} over alumina, which was activated before the start of each experiment by blowing air through it at 450° for 4 hr. For isomerization, 80 ml of olefin was taken; 60 ml of catalyst, collected after establishment of steady operation in the reactor, was subjected to rectification on an 80-theoretical-plate column. The hold-up of substance on the column packing was about 1 ml. In the fractions obtained, the specific gravity and refractive index were determined.

Table 2

Olefin	B.p., °C at 760 mm	n_D^{20}	d_4^{20}
Hexene-2-cis	68.8	1.3977	0.6869
Hexene-2-trans	67.9	1.3935	0.6784
2-Methylpentene-2	67.3	1.4004	0.6863
3-Methylpentene-2-cis	70.4	1.4045	0.6986
3-Methylpentene-2-trans	67.6	1.4016	0.6942
4-Methylpentene-2-cis	56.3	1.3880	0.6690
4-Methylpentene-2-trans	58.5	1.3889	0.6686
2,3-Dimethylbutene-2	73.2	1.4122	0.7080

The characteristics of the residue were determined after additional distillation from the flask. Table 2 gives the constants of hexenes with a deeper position of the double bonds, which could have formed upon migration of the multiple bonds in the initial olefins (*).

Table 3

Figure 1

Figure 1: Figure 1

Fraction No.	B.p., °C at 760 mm	Amount, g	n_D^{20}	d_4^{20}	Fraction No.	B.p., °C at 760 mm	Amount, g	n_D^{20}	d_4^{20}
2-Methylpentene-1					**Hexene-1**				
1	62.1—62.3	13.7	1.3922	0.6802	1	62.3—63.4	29.4	1.3880	0.6731
2	62.4—67.0	5.7	1.3965	0.6850	2	63.5—67.5	2.7	1.3909	0.6750
3	67.1—67.3	16.2	1.4007	0.6863	3	67.6—68.5	6.1	1.3962	0.6829
Residue	—	2.4	1.4015	0.6884	**3-Methylpentene-1**				
2,3-Dimethylbutene-1					1	53.7—54.3	34.0	1.3847	0.6674
1	55.3—55.4	18.1	1.3903	0.6777	2	54.4—70.4	2.8	1.3990	0.6879
2	55.8—73.0	5.3	1.4020	0.6936	Residue	—	1.5	1.4052	0.6953
3	73.1—73.2	9.3	1.4123	0.7084					
Residue	—	6.8	1.4130	0.7091					

Isomerization of 2-methylpentene-1 at a space velocity of 2.64 h^{-1}. The distillation curve (I) is shown in Fig. 1, and the characteristics of the fractions obtained are given in Table 3. Comparison of the properties of the fractions with the properties of the hexenes listed in Table 2 shows that the 1st fraction is the initial 2-methylpentene-1, while the 3rd fraction and the residue are, respectively, the substance remaining on the packing—2-methylpentene-2. Calculation of the catalyst composition from these data shows that it consists of 38% 2-methylpentene-1 and 62% 2-methylpentene-2.

Fig. 1. Distillation curves of the isomerization products at a space velocity of 2.64 h^{-1}:
I —2-methylpentene-1; **II** —2,3-dimethylbutene-1.

Fig. 2. Distillation curves of the isomerization products at a space velocity of

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

2.64 h^{-1}:
III –hexene-1; **IV** –3-methylpentene-1; **V** –4-methylpentene-1.

Isomerization of 2,3-dimethylbutene-1 at a space velocity of 2.64 h^{-1}. The distillation curve (II) is shown in Fig. 1, and the properties of the fractions are given in Table 3. A calculation made as above shows that the catalyst consists of 51% 2,3-dimethylbutene-1 and 49% 2,3-dimethylbutene-2.

Fig. 3. Distillation curves of the isomerization products at a space velocity of 0.23 h^{-1}:
VI –hexene-1; **VII** –3-methylpentene-1; **VIII** –4-methylpentene-1.

Isomerization of hexene-1, 3-methylpentene-1, and 4-methylpentene-1 at a space velocity of 2.64 h^{-1}. The distillation curves (III, IV, and V) of the catalysts for these three hydrocarbons, shown in Fig. 2, demonstrate that under these conditions they do not undergo any noticeable changes.

Isomerization of hexene-1 at a space velocity of 0.23 h^{-1}. The distillation curve (VI) is shown in Fig. 3, and the characteristics of the fractions obtained are given in Table 3. Calculation of the composition of the reaction products, made from the distillation curve and from the data in Tables 2 and 3, shows that the mixture consists of 80% of the initial hexene-1 and 20% hexenes-2.

Isomerization of 3-methylpentene-1 at a space velocity of 0.23 h^{-1}. The distillation curve (VII) is shown in Fig. 3; the characteristics of the fractions are given in Table 3. The 1st fraction is the initial 3-methylpentene-1, while the 2nd fraction and the residue are a mixture of the initial hexene with 3-methylpentene-2, the content of which in the catalyst is approximately 12%.

Isomerization of 4-methylpent-1-ene with a space feed rate of 0.23 h^{-1}. The distillation curve (VIII) is given in Fig. 3. On distillation, the starting 4-methylpent-1-ene was obtained (34.6 g), while the residue (3.0 g) had somewhat elevated constants: n_D^{20} 1.3900 and d_4^{20} 0.6769, apparently owing to the presence in it of 4-methylpent-2-ene, whose content in the catalyzate does not exceed 4%.

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Received
28 IX 1959

References Cited

[1] I. I. Ioffe, S. Z. Roginskii, ZhFKh, 31, 612 (1957). [2] H. Dunning, Ind. Eng. Chem., 45, 551 (1953). [3] I. V. Gostunskaya, N. I. Tyun’ kina, B. A. Kazanskii, DAN, 108, 473 (1956). [4] F. Whitmore, Chem. and Eng. News, 26, 668 (1948); *Synthesis of Motor Fuel*, Coll. 1, IL, 1949, p. 7. [5] A. Oblad, J. Messenger, N. Brown, Ind. Eng. Chem., 39, 1462 (1947); *Synthesis of Motor Fuel*, Coll. 1, IL, 1949, p. 72. [6] F. D. Rossini et al., *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Pittsburgh, 1953.

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