ORGANIC CHEMISTRY

DEHYDRATION OF 2-METHYL-2-BUTANOL ON ZEOLITES

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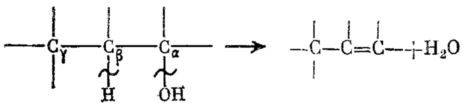
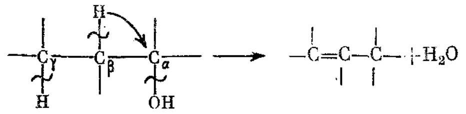
The dehydration of alcohols can take place by splitting H atoms not only from β-carbon atoms (β-elimination) but also from γ-carbon atoms (γ-elimination):

Scheme 1



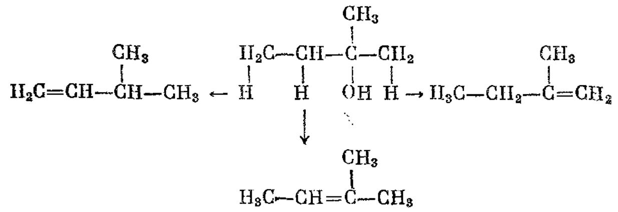
β-Elimination



γ-Elimination

Significant yields of γ-elimination products occur on the dehydration of primary alcohols or alcohols that do not contain H atoms on the β-carbon atoms [1-3]. According to [3], when alcohols are dehydrated on ThO_2 and Al_2O_3 with different Na ion contents, γ-elimination becomes more important as the basicity of the catalyst increases. In order to determine whether γ-elimination depends on the acidity of the catalyst as well as on its basicity, we studied the dehydration of 2-methyl-2-butanol (MBOL) on zeolites NaY, CaY, HY, and on an extremely high-silica zeolite (EHSZ). Dehydration of MBOL can result in 2-methyl-1-butene, 2-methyl-2-butene, and 3-methyl-1-butene (3M1B); the first two alkenes are formed by a β-elimination mechanism and 3M1B is formed by a γ-elimination mechanism:

Scheme 2



Dehydration of alcohols is known to be accompanied often by a secondary reaction in which the C = C bond is shifted, which makes the study of the direction of dehdration more complicated. We therefore selected MBOL because its dehydration product by γ-elimination is 3M1B, whose equilibrium concentration is <2% in methylbutenes at 100-200°C. The formation of 3M1B in an amount greater than 2% of the methylbutene yield cannot be the result of a secondary isomerization reaction.

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TABLE 1. Dehydration of 2-Methyl-2-butanol

Catalyst	Rate of alcohol feed, g/g catalyst	Alcohol conversion, %, at, °C				
		120	140	160	180	200
NaY	2,54	0,2	1,0	4,1	16,3	37,2
EHSZ	1,88	1,0	7,3	25,1	42,0	90,4
CaNaY	2,44	84,6	98,6	100	100	100
HNaY	8,91	93,5	97,1	99,0	99,3	100

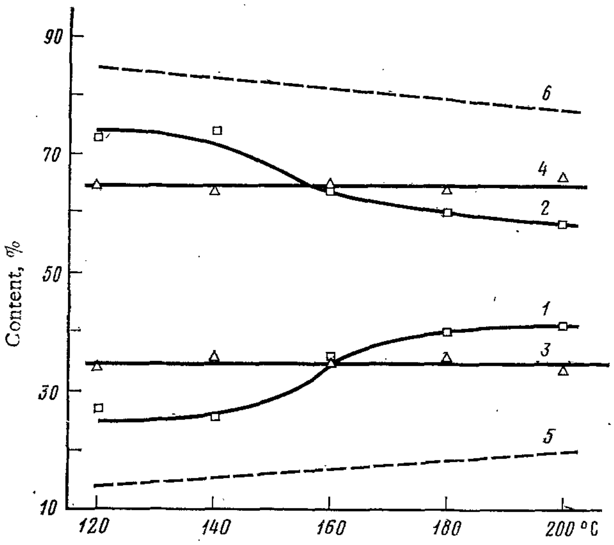


Fig. 1. Effect of reaction temperature on the methylbutene ratio in the dehydration of 2-methyl-2-butanol on NaY (1, 2) and on the extremely high-silica zeolite (3, 4). 1, 3) 2-Methyl-1-butene; 2, 4) 2-methyl-2-butene. The dashed lines represent the equilibrium content of 2-methyl-1-butene (5) and 2-methyl-2-butene (6) in the methylbutene mixture.

EXPERIMENTAL

The tests were performed in a continuous-flow device in a current of He at atmospheric pressure. The alcohol was fed in at 3.8 ml/h. The He : alcohol molar ratio was 3. The degree of exchange was 80% in zeolites CaY and HY. Zeolite Y had a $SiO_2 : Al_2O_3$ ratio $\simeq 4$. The factory-supplied batch of EHSZ was prepared with tetrabutylammonium bromide and had a modulus of 60. The catalyst was treated with air at 500°C before each test (HY at 400°C) for 4 h and then for 2 h with helium. The amount of NaY catalyst was 1.2 g, EHSZ 1.7 g, CaY 1.3 g, HY 0.4 g. The reaction products were condensed at −78°C and analyzed on a chromatograph equipped with a flame-ionization detector and stainless-steel columns (3 mm in diameter), N_2 carrier-gas velocity 30 ml/min. The composition of the alkenes was determined at ~20°C in a column 6 m long filled with 15% polypropylene glycol-425 on Chromosorb W. The alkene yield was determined at 80°C in a column 3 m long with 20% Carbowax 15M on Chromaton N.

DISCUSSION OF RESULTS

The data of Table 1 indicate that the MBOL dehydration activity of the zeolites studied increases in the order: NaY < EHSZ < CaY < HY. γ-Elimination in the alcohol occurs in the same order as the catalyst activity. When the reaction was carried out on NaY, no γ-elimination product was detected; on EHSZ, only traces of 3M1B were found; and the 3M1B content of the methylbutenes was ~ 15% on CaY and HY at 180°C (Figs. 1-3). It is generally considered that the heterogeneous dehydration of alcohols occurs through OH splitting by the acidic center (A) and the H atom eliminated is coordinated with the basic center (B) [4-7]. The conclusion was reached in [1, 3, 5, 7, 8] that an electron-density shift takes place between the A and B centers, on the one hand, and the adsorbate, on the other:

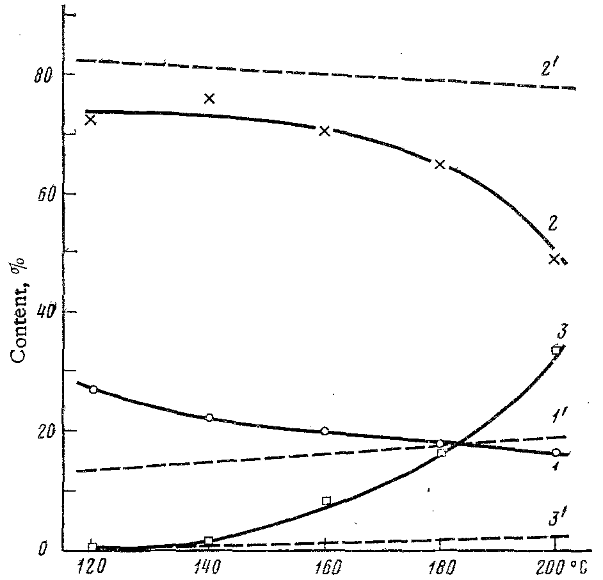
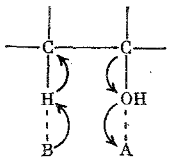


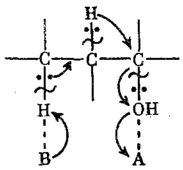
Fig. 2. Effect of reaction temperature on the methylbutene ratio in the dehydration of 2-methyl-2-butanol on CaY. 1) 2-Methyl-1-butene; 2) 2-methyl-2-butene; 3) 3-methyl-1-butene. The dashed lines represent the equilibrium alkene content (1'-3') in the methylbutene mixture.

Scheme 3



It is natural to suppose that the considerable electron-density shift is not limited by the β-C atom when there is enough acid-center strength, but also extends to the γ-C atom. Such an electron-density shift opens up the possibility of a β-center interaction not only with the H atom on the β-C atom, but also with the one on the γ-C atom:

Scheme 4



Unlike NaY, zeolites CaY and HY possess considerable acidity [9]. Consequently, the formation of a γ-elimination product in the dehydration of MBOL on CaY and HY and its absence on NaY is due to the difference in the strength of the acidic centers of these zeolites.

The electron-density shift shown in Schemes 3 and 4 is evidently due not only to the acidic centers A but also to the basic centers B, which apparently explains the higher γ-elimination product yield observed in [3] as the catalyst's basicity is increased.

When the reaction is carried out on CaY and HY, the content of the γ-elimination product, 3M1B, in the methylbutenes formed increases with the temperature of the tests from 120 to 200°C (see Figs. 2 and 3). β-Elimination proceeds with rupture of one C—H bond, whereas in γ-elimination two C—H bonds must be broken and an H—atom must be shifted (see Schemes 1 and 4). Thus, more reactive molecules are needed for γ-elimination than for β-elimination. Increasing the reaction temperature increases the reactivity of the alcohol

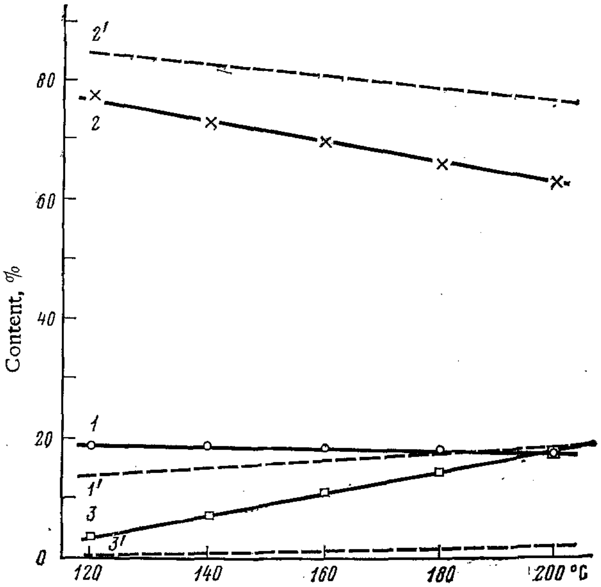


Fig. 3. Effect of reaction temperature on methylbutene ratio in the dehydration of 2-methyl-2-butanol on zeolite HY. The notation is given in Fig. 2.

molecules and therefore the fraction of molecules reacting by the γ-elimination mechanism. The significant γ-elimination product yield observed in [1-3] in the dehydration of primary alcohols and alcohols without H atoms on the β-C atom over Al_2O_3 was apparently caused by the relatively high reaction temperature (275-350°C) necessary to dehydrate alcohols with such a structure. On the other hand, the dehydration of secondary and tertiary alcohols on Al_2O_3 usually proceeds at lower temperatures [5, 7], probably because γ-elimination products are not formed when they are dehydrated.

A comparison of the results obtained with data from [3] indicates that the dehydration of alcohols by a γ-elimination mechanism requires both pairs of acidic and basic catalyst centers and high reactivity in the alcohol molecule.

CONCLUSIONS

1. The activity of the zeolites studied in the dehydration of 2-methyl-2-butanol between 120 and 200°C increases in the following order: NaY < EHSZ < CaY < HY.

2. The content of the γ-elimination product in the methylbutenes formed on dehydration of 2-methyl-2-butanol (3-methyl-1-butene) increases with the catalyst's activity and the reaction temperature.

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