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NOTES

Catalytical Dehydration of Aliphatic Alcohols on $\gamma - Al_2O_3$

Dohse (*1*) and more recently Stauffer and Kranich (*2*) investigated the influence of the substrate structure on the activation energy for the dehydration of aliphatic alcohols. The results of these authors are not in complete agreement.

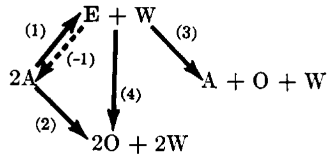
Before comparing activation energies, it must be ascertained that the conditions of the reactions to be observed are similar. The mechanisms must also be comparable. It is therefore necessary to determine the reaction scheme, which then shows whether further comparison of the reactions is possible. We have investigated the elimination of water from the primary alcohols methanol to hexanol and from the branched C_3 and C_4 isomers on $\gamma - Al_2O_3$.

EXPERIMENTAL

The measurements were made using a gas chromatograph and a differential flow reactor (*3*) in a temperature range of 120° to 310°C. The alumina, defined according to Schwab and co-workers (*4*) as γ phase, proved to be fully selective for the dehydration and could easily be prepared with reproducible activity.

RESULTS AND DISCUSSION

Straight-chain aliphatic (primary) alcohols (A). In the investigated temperature range between 120° and 310°C methanol yields solely dimethyl ether and water. With the remaining alcohols, ether (E), water (W), and olefin (O) are the products. The ether concentrations show definite maxima with respect not only to the contact temperature but also to the retention times. This points to the presence of a consecutive reaction, with ether as the primary product. In the second stage, depending on the temperature, the ether reacts further to give olefin, either through water elimination or through a reformation of alcohol. The lack of an induction period in the time curves of the olefin points to a parallel direct olefin formation at higher temperatures. The following general scheme for the primary alcohols can be put forward:



A comparison of the values of the free enthalpies and the experimental results shows that at low temperatures the thermodynamically less favorable bimolecular ether formation is preferred. This is also true for the decomposition of the ether according to reaction (3) as compared to (4). Increasing temperature moves the reaction, also on $\gamma - Al_2O_3$, in the direction of the thermodynamically favored products. Increasing chain length tends to favor the direct olefin elimination at the cost of the ether formation.

At low temperatures and a small degree of conversion the equilibrium reaction (—1) and the direct olefin formation (2) are negligible, so that by choosing the proper conditions, the primary step (1) can be isolated for all the primary aliphatic alcohols on $\gamma - Al_2O_3$. This step is bimolecular and since the reaction order $n = 0$ can be found, presumably is a Langmuir-Hinshelwood mechanism.

The olefins, formed either in a primary step according to (2) or in secondary steps according to (3) and (4), always have the double bond in the end position. These products can then isomerize further. Skeletal isomerization takes place only to a small extent.

Branched aliphatic alcohols. From the values of the free reaction enthalpies, it can be shown that the ether formation from these alcohols is thermodynamically less favorable than for the unbranched alcohols. In fact, a small ether concentration can be proved only for isopropanol, while simultaneously olefin is formed directly. From isobutanol and tertiary butanol the only product is isobutylene. The dehydration of secondary butanol gives, in apparently parallel steps, 1-butene, as well as *cis*- and *trans*-2-butene. The formation of the *cis* product is here greatly preferred.

If the "principle of least motion" is valid, then, because of the comparable product distribution, a comparison with regard to the mechanism of similar reaction stages for the various alcohols may be concluded, with a certain degree of probability, even without an exact knowledge of the actual reaction mechanism and the elementary steps.

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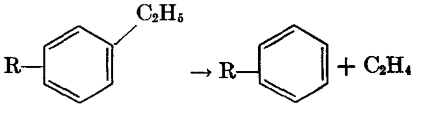
Correlation of Reactivity and Adsorptivity of Ethylbenzene and Ethyltoluenes

The gas chromatographic method allows study of the adsorption of substrates on solid catalysts at actual reaction conditions (*1–4*). One of the points of interest in conducting these measurements is the comparison of adsorptivity and reactivity of isomeric or homologous compounds, i.e. the comparison of structure effects on adsorption properties and reaction ability.

In studying the transformations of ethylbenzene and three isomeric ethyltoluenes on an acidic catalyst (*5*) we have obtained good correlation between dealkylation rates and retention times. The catalyst which was prepared by impregnation of alumina with an aluminum fluoroborate solution (*6*) has catalytic properties in many respects similar to silica-alumina (*7*). The rate of dealkylation [Eq. (1)] was determined at 400°C



(1)

R = H, *o*-CH_3, *m*-CH_3, *p*-CH_3