AN INVESTIGATION OF THE DEHYDRATION OF 3-OXA-, 3-THIA- AND 3-AZA-1,5-PENTANEDIOLS IN THE PRESENCE OF TRICALCIUM PHOSPHATE

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In the presence of tricalcium phosphate, 3-oxa-, 3-aza-, and 3-thia-1, 5-pentanediols undergo intramolecular dehydration with the formation of heterocycles and also of unstable readily-polymerizing vinyl compounds. The total degree of conversion of the diols rises in the sequence diethyleneglycol < 1, 5-pentanediol < diethanolamine < N-methylethanolamine < di(hydroxyethyl) sulfide. At low temperatures, the yield of cyclic product from 1, 5-pentanediol and diethyleneglycol is close to the degree of conversion of the diol, and at high temperatures it falls behind markedly. Diethanolamine, N-methyldiethanolamine, and di(hydroxyethyl) sulfide dehydrate to the corresponding six-membered oxides unselectively.

In preceding papers it was shown that one of the factors determining the rate and direction of catalytic dehydration is the structure of the diol [1-3].

Thus, the presence of a C=C double bond in the molecule of 2-butene-1, 4-diol accelerates its intramolecular dehydration in comparison with that of 1,4-butanediol; the trans-form of the butenediol dehydrates more readily than the cis-isomer [3].

In the present work, we studied the dehydration of 1,5-pentanediols containing in position 3, besides a carbon atom, the heteroatoms O, N, and S in the presence of an active and selective dehydration catalyst-tricalcium phosphate.

It has been reported [4] that when diethyleneglycol is heated in contact with an aluminosilicate at 200° C 1, 4-dioxane is formed with a yield of 88.5%.

The main products of the transformation of diethyleneglycol in the presence of a synthetic aluminosilicate at 250-400° C are dioxane, ethyleneglycol acetal, acetaldehyde, paraldehyde, and acetic acid [5]. At 350° C the yields of dioxane and acetaldehyde are 32.2 and 35.0% and at 400° C the amount of water liberated corresponds to the degree of dehydation of the diol—78.8%. The hypothesis has been put forward [5] that the acetaldehyde is obtained via an intermediate stage of the formation of dioxane.

According to the patent literature [6], in the dehydration of diethanolamine in the presence of oleum at $200-235^{\circ}$ C the yield of morpholine reaches 95%. Di(hydroxyethyl) sulfide dehydrates to 1,4-thioxane on being heated with potassium bisulfite with a yield of 52% [7] and in the presence of ion-exchange resins with a yield of 56% [8].

From the figures given it can be seen that the dehydration of the 1,5-diols containing heteroatoms has been studied inadequately.

EXPERIMENTAL

The reactions were carried out in the vapor phase under continuous conditions at atmospheric pressure. The tricalcium phosphate was obtained by the preciptation method [9]. A vertical quartz tube was charged with 5 ml of the catalyst (granules with a diameter of 2-3 mm). Above the layer of catalyst was placed 5 ml of broken quartz. After each experiment, the catalyst was regenerated in a current of hydrogen at 400-450 \degree C for 1 hr 30 min-2 hr.

The work was carried out with commercial samples of the diols the constants of which corresponded to literature data. It was found chromatographically that the contents of impurities in them did not exceed 1.5-2%. The starting materials were fed uniformly into the reactor at a space velocity of 1 hr^{-1} with an automatic dosing device.

The reaction products were analyzed by gas-liquid chromatography using a katharometer detector. The yields of the reaction products were determined by means of internal standards. The catalyzates obtained in the dehydration of the diols contained low-boiling hydrocarbons, heterocyclic compounds, and high-boiling unchanged diols. The contents of these compounds in the catalyzate were determined on three columns under various conditions.

The analysis of the low-boiling substances was carried out in a column 8 m long (15% of β , β '-oxydipropionitrile on washed diatomite brick) at 20-50°C. The rate of flow of the carrier gas, helium, was 40-50 ml/min. The internal standard was n-heptane.

The heterocyclic compounds were analyzed on a column 2.5 m long containing polyethyleneglycol (mol. wt. 4000) on Celite at 80-90°C. The internal standard was n-butanol.

The analysis of the high-boiling diols was carried out at $160-165^{\circ}$ C on a column 6 m long containing polyethyleneglycol (mol. wt. 4000) and 1 and 0.5% of KOH on NaCl (0.25-0.5 mm fraction). The rate of flow of the carrier gas was 20-60 ml/min. The internal standard was ethylene glycol [10].

The figure gives the results of experiments on the conversion of 1, 5-pentanediol, diethyleneglycol, diethanolamine, N-methyldiethanolamine, and di(hydroxyethyl) sulfide at 325, 350, and 375°C. A comparison of the results obtained shows that the degree of conversion in the presence of calcium phosphate of the 1, 5-diols studied depends on the nature of the heteroatom. Thus, in experiments at 320°C the degree of conversion of 1, 5-pentanediol was 70% and that of diethyleneglycol 18%.

In contrast to this, the replacement of the $-CH_2$ -group in the molecule of the 1,5-diol by > NH or > N--CH₃ markedly raised the reactivity of the diol. For example, the degree of conversion of diethanolamine at 325° C (80%) was 2.5 times greater than that of 1,5-pentanediol (30%). The degree of conversion in the presence of calcium phosphate of the diols studied rises in the following sequence: diethyleneglycol < 1,5-pentanediol < diethanolamine < N-methyldiethanolamine < di(hydroxyethyl) sulfide.

The catalytic nature of the conversions studied is confirmed by the fact that, for example, 1,5-pentanediol undergoes no change on being passed through the tube at 423° C in the absence of the catalyst.

The main products of the catalytic dehydration of the diols are the corresponding cyclic compounds. Two routes for the formation of cyclic products in the processes studied are possible.





Influence of the heteroatom in the molecule of a 1,5-diol on the degree of conversion (1) and the yield (2) of the corresponding six-membered oxide at 325, 350, and 375° C.

Apparently, the process in which both OH groups of the molecule undergoing conversion participate (2) predominates.

This is confirmed by the fact that on the phosphate catalyst 4-penten-1-ol undergoes cyclization only to the extent of 2.5-4.6% while 1, 5-pentanediol does so to the extent of 53.6%. Moreover, in the cyclization of 1, 5-pentanediol the main product is tetrahydropyran, while the pentenol gives mainly α -methyltetrahydrofuran. These facts permit the assumption that the cyclic products are formed directly from the diols (2) and not through the intermediate stage of an unsaturated compound (1). At 325° C, 1, 5-pentanediol and diethyleneglycol dehydrogenate selectively: the degree of conversion and the yield of the oxide practically coincide. However, when the temperature of the reaction is raised the yield of oxide formed begins to lag behind the degree of conversion of the diol. At 375° C, the degree of conversion of diethyleneglycol is approximately three times greater than the yield of dioxane (figure).

In the dehydration of diethanolamine and N-methyldiethanolamine, even at 325° C the degree of conversion of the diols considerably exceeds the yields of, respectively, morpholine and N-methylmorpholine. A similar influence of the temperature is observed in the dehydration of di(hydroxyethyl) sulfide (375°C).

The decrease in the selectivity of the dehydration of the diols to six-membered oxides cannot be explained by their low stability. Special experiments showed that dioxane and morpholine undergo practically no change at 350°C, while tetrahydropyran undergoes only 7.2% conversion into pentadienes.

Thus, the relatively low yield of oxides is explained not by low stability but by the fact that at the elevated temperature the diols begin to undergo conversion in other directions. It may be assumed that the 1, 5-diols containing heteroatoms dehydrate with the formation of readily-polymerizing vinyl compounds.

polymerization

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When diethyleneglycol was passed through the apparatus at 375° C, acetaldehyde was obtained with yield of 5.5%. In the process

under investigation acetaldehyde is probably produced via the intermediate formation of the monovinyl ether of ethylene glycol

$$\begin{smallmatrix} \mathsf{C}\mathsf{H}_2-\mathsf{C}\mathsf{H}_2-\mathsf{O}\mathsf{-}\mathsf{C}\mathsf{H}_2-\mathsf{C}\mathsf{H}_2\\ \mathsf{O}\mathsf{H} & \mathsf{O}\mathsf{H} \end{smallmatrix} \longrightarrow \begin{bmatrix} \mathsf{C}\mathsf{H}_2-\mathsf{C}\mathsf{H}-\mathsf{O}-\mathsf{C}\mathsf{H}_2-\mathsf{C}\mathsf{H}_2\\ \mathsf{O}\mathsf{H} \\ \mathsf{O}\mathsf{H} \end{bmatrix} \twoheadrightarrow {}^2\mathsf{C}\mathsf{H}_3-\mathsf{C} \overset{\mathsf{O}}{\overset{\mathsf{O}}}_{\mathsf{H}}$$

In the dehydration of diethanolamine and N-methyldiethanolamine the amount of water liberated corresponded approximately to the degree of conversion of the diols. For example, at 325° C the degree of diethanolamine was 72.5% and the yield of water 65%. At the same time, there was a marked deposition of carbon on the catalyst and a small amount of acetaldehyde (1-2%) was formed.

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