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Abstract

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ON THE ISOMERIZATION AND DEHYDROGENATION REACTIONS OF THE TETRAHYDROFURAN RING

One of the problems in the field of dehydrogenation catalysis is the study of the possibility of dehydrogenating five-membered heterocycles—pyrrolidine, thiophane, and tetrahydrofuran—into the corresponding unsaturated heterocycles.

In the works of Zelinskii and Yur' ev [1,2] it was shown that pyrrolidine and thiophane are capable of being dehydrogenated on platinum and palladium in the vapor phase to pyrrole and thiophene, respectively. The behavior of tetrahydrofuran proved unexpected. An attempt to carry out its dehydrogenation in the vapor phase over a platinum catalyst was unsuccessful [3]. It was difficult to find an explanation for such a sharply different relation to the dehydrogenation reaction of pyrrolidine and thiophane, on the one hand, and tetrahydrofuran, on the other. Until very recently there were no experimental data that could provide a basis for explaining this interesting fact. In 1958 the reaction of isomerization of tetrahydrofurans into aliphatic carbonyl compounds was discovered [4]. This discovery was directly related to the dehydrogenation reaction of the tetrahydrofuran ring. The ease with which the latter is isomerized on platinum into carbonyl compounds already at 230-250° shows why it is practically impossible on this catalyst to carry out the dehydrogenation reaction of tetrahydrofuran. It became clear that the negative results obtained on platinum with respect to the dehydrogenation of tetrahydrofuran can be explained by its capacity for the isomerization reaction, which on this catalyst proceeds at a considerably higher rate than the dehydrogenation reaction of the tetrahydrofuran nucleus. This circumstance again raised the problem of dehydrogenation of the tetrahydrofuran ring, but now in a more definite sense. The investigation was reduced to the search for such catalysts on which the rates of both reactions—isomerization and dehydrogenation of the tetrahydrofuran ring—would be practically commensurate. This condition has very broad limits, since various groups of catalysts may prove suitable for this purpose. We investigated the action on the tetrahydrofuran ring of rhodium, osmium, iridium, and ruthenium deposited on activated carbon. These catalysts are in many respects analogous to platinum, but at the same time sometimes differ from it in essential properties. Since the purpose of our investigation was to follow the course on catalysts of the isomerization and dehydrogenation reactions of the tetrahydrofuran ring, it seemed more convenient to use tetrahydrosylvan for this purpose, which as a result of both reactions gives liquid products: pentanone-2 and sylvan. The reaction was carried out at 300–400°. The principal result of our experiment is as follows: rhodium, osmium, iridium, and ruthenium, like platinum, carry out predominantly the isomerization reaction of the tetrahydrofuran ring; however, unlike platinum, this is not the only reaction that takes place on these catalysts. To a fairly considerable extent there proceeds

and the dehydrogenation reaction of the tetrahydrofuran ring, as a result of which silvane is formed from tetrahydrosilvane.

$$\text{2-methyltetrahydrofuran} \xrightarrow{\text{isomerization}} \mathrm{CH_3CH_2CH_2{-}C(=O){-}CH_3}$$

$$\text{2-methyltetrahydrofuran} \xrightarrow{\text{dehydrogenation}} \text{2-methylfuran} + 2\mathrm{H_2}$$

The relative content of silvane and methyl propyl ketone in the reaction products is practically independent of the temperature, which, as was to be expected, changes only the overall conversion of tetrahydrosilvane. The degree of conversion of tetrahydrosilvane into silvane and methyl propyl ketone at 350–400° amounted, on average over all catalysts, to 50–70%. If the amounts of the silvane and methyl propyl ketone formed are related to the amount of tetrahydrosilvane converted, the following is obtained: 15–20% silvane is formed, and 65–70% methyl propyl ketone.

It is quite probable that the use of other catalysts will make it possible to carry out the dehydrogenation reaction of the tetrahydrofuran ring in a more directed manner.

In the present work catalysts prepared by depositing certain metals of the eighth group of the periodic system on activated carbon were investigated. The method of their preparation was as follows: activated carbon was impregnated with an aqueous solution of OsO_4, H_2IrCl_6, $RuCl_4$, and $RhCl_3$, and then these compounds were reduced with hydrogen in a reaction tube at temperatures of 200–300°. The catalysts prepared in this way contained about 5% active finely dispersed metal.

Tetrahydrosilvane was obtained by hydrogenating silvane in an autoclave over a skeletal nickel-aluminum catalyst at 100–120°. It had the following properties: b.p. 79–79.5° at 750 mm; d_4^{20} 0.8520; n_D^{20} 1.4060. Tetrahydrosilvane was passed over the catalyst at a space velocity of ~ 0.1 h^{-1}. The catalyzates were fractionated on an efficient column; the silvane and methyl propyl ketone isolated in this way were identified by determining their physical constants: silvane, b.p. 62–64°; d_4^{20} 0.9118; n_D^{20} 1.4318; methyl propyl ketone, b.p. 100–101.5°; d_4^{20} 0.8080; n_D^{20} 1.3912.

Conclusions. 1. The fundamental possibility has been demonstrated of dehydrogenating the tetrahydrofuran ring to the furan ring at 350–400° in the presence of Rh, Ir, Os, and Ru deposited on activated carbon.

2. Under these conditions, in parallel with the dehydrogenation reaction of the tetrahydrofuran nucleus, its isomerization proceeds with the formation of aliphatic carbonyl compounds. The latter reaction is the principal one.

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