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Abstract

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CATALYTIC DEHYDROGENATION OF DIHYDROFURANS

2,3- and 2,5-dihydrofurans under thermal conditions undergo transformations in sharply different directions. For example, 2-methyl-4,5-dihydrofuran at 470–480° isomerizes to methyl cyclopropyl ketone ([1]), whereas 2-methyl-2,5-dihydrofuran under analogous conditions undergoes dehydrogenation to 2-methylfuran ([2]):

$$\text{2-methyl-4,5-dihydrofuran} \xrightarrow{470\text{–}480^\circ} \text{methyl cyclopropyl ketone}$$

$$\text{2-methyl-2,5-dihydrofuran} \xrightarrow{470\text{–}480^\circ} \text{2-methylfuran} + H_2$$

Both of these reactions evidently have a common character. For the second of them it has been shown that various 2-alkyl-2,5-dihydrofurans can undergo dehydrogenation to the corresponding homologs of furan ([2]).

Wilson ([3]), who observed the isomerization reaction of 2,3-dihydrofuran to cyclopropanecarboxaldehyde under thermal conditions, investigated the effect of various contacts on this reaction, but did not find any appreciable catalytic effect. The discovery of the possibility that the dehydrogenation reaction of 2,5-dihydrofurans proceeds under thermal conditions made broader the task of finding catalysts, since it was not excluded that the catalytic action of suitable contacts might appear with respect to the dehydrogenation reaction of dihydrofurans. In particular, for 2,5-dihydrofurans the problem of catalysis came down to carrying out, in the presence of catalysts, the dehydrogenation reaction that proceeds under thermal conditions. For 2,3-dihydrofurans only one type of transformation was known, namely, their isomerization to cyclopropane carbonyl compounds. Therefore, in this case a more general question arose: whether, under certain conditions and under the action of catalysts, it is also possible to carry out the dehydrogenation reaction of dihydrofurans of this series to the corresponding furan compounds. In the present study answers to these questions are given. We fixed our choice on platinum and palladium—metals whose catalytic properties with respect to hydrogenation and isomerization reactions of furan and tetrahydrofuran compounds had been investigated by us earlier.

It could be expected in advance that, in contrast to the dehydrogenation reaction of dihydrofurans under thermal conditions, other processes would occur on catalysts, associated with the ability of these catalysts to add hydrogen to furan and dihydrofuran rings, to carry out hydrogenolysis of the furan nucleus, and to bring about isomerization of tetrahydrofurans into aliphatic carbonyl compounds. Taking all these circumstances into account, we were able without particular difficulty to form a clear picture of the successive reactions taking place on platinum and palladium when vapors of 2,3- and 2,5-dihydrofurans are passed over them.

The principal result of our investigation is as follows: both 2,5- and 2,3-dihydrofurans on platinum and palladium catalysts in the temperature range 200-300° undergo only dehydrogenation to the corresponding homologs of furan. The composition of the reaction products changes depending on the temperature, since the latter promotes either hydrogenation of the furan ring or its hydrogenolysis.

On a platinum catalyst at 300° a study was made of the transformations of 2-methyl-4,5-dihydrofuran and 2-ethyl-2,5-dihydrofuran. As a re-

as a result, approximately equal amounts were obtained: from the first—sylvan and 2-pentanone, and from the second—α-ethylfuran and 3-hexanone. This result can be explained as follows: first, dehydrogenation of the dihydrofurans to the corresponding furan compounds takes place; the hydrogen evolved in this process can hydrogenate dihydrofurans to tetrahydrofurans or carry out hydrogenolysis of the furan ring. If the catalyst and temperature favor isomerization of tetrahydrofurans to aliphatic ketones, then the final products in this case are only furan compounds and an aliphatic ketone:

$$\text{2-methyl-4,5-dihydrofuran} \xrightarrow{\text{Pt–C}} \text{sylvan} + \text{H}_2,$$

$$\text{2-methyl-4,5-dihydrofuran} \xrightarrow{\text{H}_2,\ \text{Pt–C}} \text{2-methyltetrahydrofuran} \xrightarrow{\text{Pt–C}} \text{C–C–C–C(=O)–C} \quad (4),$$

$$\text{2-methyl-4,5-dihydrofuran} \xrightarrow{2\text{H}_2,\ \text{Pt–C}} \text{C–C–C(=O)–C} \quad (5).$$

Exactly the same transformations occur on a palladium catalyst at 300°. Here, however, it was necessary to prove the possibility of isomerization of tetrahydrofurans into aliphatic carbonyl compounds. Specially designed experiments, in which tetrahydrosylvan was passed over a palladium catalyst at 300°, convinced us that tetrahydrosylvan is indeed isomerized to methyl propyl ketone, although to a considerably weaker extent than on platinum. The weak isomerizing properties of palladium, as well as its enhanced ability to hydrogenate double bonds in the furan ring, lead to the fact that dihydrofurans on a palladium catalyst at 200° are converted into a mixture of equimolar amounts of the corresponding furan and tetrahydrofuran compounds:

$$2\,\text{2-methyl-4,5-dihydrofuran} \xrightarrow{\text{Pd–C, } 200^\circ} \text{sylvan} + \text{tetrahydrosylvan}.$$

In this case the analogy is manifested especially clearly between the conversion of dihydrofurans into furans and tetrahydrofurans and the "irreversible" catalysis of cyclohexenes and cyclohexadienes. In conclusion, one interesting fact should be noted concerning the properties of hydrogen adsorbed on the surface of platinum and palladium catalysts. The platinum catalyst (10% Pt) was prepared by impregnating activated charcoal with a solution of chloroplatinic acid, which was reduced with formalin in the presence of caustic alkali. Such a catalyst contained a significant amount of hydrogen, which either hydrogenated dihydrofurans to tetrahydrofurans or carried out hydrogenolysis of the furan ring. As a result, the first portions of dihydrofuran gave catalyzates containing, in comparison with equimolar amounts, larger quantities of aliphatic ketone. Conversely, hydrogen adsorbed by a palladium catalyst during the reduction with hydrogen of palladium chloride deposited on charcoal (10% Pd) does not show appreciable ability to hydrogenate dihydrofurans or to carry out hydrogenolysis of the furan ring. Therefore, the catalyzates of dihydrofurans obtained on palladized charcoal, from the very first portions, contained equimolar mixtures of furans and tetrahydrofurans, or (at a higher temperature) furans and aliphatic ketones. It seems to us that further studies in this direction could provide additional information on the properties of adsorbed hydrogen.

Experimental Part

2-Methyl-4,5-dihydrofuran was obtained by dehydration of acetopropyl alcohol in the presence of phosphoric acid. 2-Ethyl-2,5-dihydrofuran

was synthesized according to the following scheme:

[[chemical scheme: tetrahydrofuran]] $\xrightarrow{Cl_2}$ [[chemical scheme: dichlorotetrahydrofuran]] $\xrightarrow{C_2H_5MgBr}$ [[chemical sc

2-Ethyl-3-chlorotetrahydrofuran was slowly added to caustic potash heated to 180–200°, with immediate distillation of the 2-ethyl-2,5-dihydrofuran formed.

After distillation on an efficient column, the dihydrofurans had the following properties:
1) 2-methyl-4,5-dihydrofuran; b.p. 79–80° at 752 mm; d_4^{20} 0.9040; n_D^{20} 1.4298;
2) 2-ethyl-2,5-dihydrofuran; b.p. 104–104.5° at 755 mm; d_4^{20} 0.8877; n_D^{20} 1.4314.

The initial dihydrofurans were fed onto the catalyst at a space velocity of 0.1 hr^{-1}. The liquid catalyzates, obtained in practically theoretical amounts, were fractionated on a column. The results of the experiments are given in Table 1.

Table 1

Products of the transformations of 2-methyl-4,5-dihydrofuran and 2-ethyl-2,5-dihydrofuran on Pt–C and Pd–C catalysts

Initial substance	Catalyst	Temp., °C	Reaction products and their properties: composition of catalyzate	Yield, %	b.p., °C	d_4^{20}	n_D^{20}
2-Methyl-4,5-dihydrofuran	Pt—C	300	Silvan	50	62–64	0.9118	1.4321
2-Methyl-4,5-dihydrofuran	Pt—C	300	Pentanone-2	50	100–101.5	0.8080	1.3910
2-Methyl-4,5-dihydrofuran	Pt—C	200	Silvan	50			
2-Methyl-4,5-dihydrofuran	Pt—C	200	Tetrahydrosilvan	30			
2-Methyl-4,5-dihydrofuran	Pt—C	200	Pentanone-2	20			
2-Ethyl-2,5-dihydrofuran	Pt—C	300	α-Ethylfuran	40	91–91.5	0.9018	1.4404
2-Ethyl-2,5-dihydrofuran	Pt—C	300	Hexanone-3	40	123–124	0.9169	1.4006

Initial substance	Catalyst	Temp., °C	Reaction products and their properties: composition of catalyzate	Yield, %	b.p., °C	d_4^{20}	n_D^{20}
2-Methyl-4,5-dihydrofuran	Pd—C	200	Silvan	50			
2-Methyl-4,5-dihydrofuran	Pd—C	200	Tetrahydrosilvan	50	79–80	0.7582	1.4060
2-Methyl-4,5-dihydrofuran	Pd—C	300	Silvan	50			
2-Methyl-4,5-dihydrofuran	Pd—C	300	Pentanone-2	50			
2-Ethyl-2,5-dihydrofuran	Pd—C	300	α-Ethylfuran	40			
2-Ethyl-2,5-dihydrofuran	Pd—C	300	Hexanone-3	30			

Conclusions. 1. It has been established that both 2,5- and 2,3-dihydrofurans, on Pt and Pd deposited on activated carbon, undergo dehydrogenation at 200-300° to the corresponding furans. The hydrogen evolved in this process reacts with furans and dihydrofurans, forming the corresponding tetrahydrofurans and aliphatic ketones.

2. On Pd-carbon at 200°, the conversion of 2-methyl-4,5-dihydrofuran into equimolar amounts of silvan and tetrahydrosilvan indicates the analogy of

this reaction with an irreversible catalysis.

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