

HETEROGENEOUS CATALYTIC OXIDATION OF FURFURYL ALCOHOL AND BENZYL ALCOHOL IN THE GAS PHASE IN A REACTOR FILLED WITH LEAD OXIDE

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The oxidative decarboxylation reaction of furfuryl and benzyl alcohols in the presence of lead oxide has been studied. It has been established that in the course of oxidative decarboxylation of furfuryl alcohol, furane and pyrophoric lead are formed. The oxidative decarboxylation of benzyl alcohol at different temperatures resulted in benzene, benzaldehyde and toluene. The increase of temperature favours benzene formation while the amount of toluene decreases.

In our previous papers [1—4] it has been shown that lead oxide is a suitable catalyst for realizing the oxidative decarboxylation of furfural to furane. The decarboxylation of benzoic acid to benzene is known [5, 6] and several authors have dealt with the heterogeneous catalytic preparation of benzyl alcohol and furfuryl alcohol in gas phase. SABATIER and his coworkers [7, 8] observed that on aluminium oxide catalyst benzyl alcohol yields a resinous product, however, the formed substances have not been studied yet. The formation of dibenzyl ether on the former catalyst has been described as well as the decomposition of this product into toluene and benzaldehyde by ADKINS and FOKERS [9]. According to BARTÓK's [10, 11] investigations benzyl alcohol at lower temperatures yields dibenzyl ether, which undergoing intramolecular dehydrohydrogenation at higher temperature results in toluene and benzaldehyde. The decomposition of dibenzyl ether has been first described by CANNIZZARO, LOWE and ODDO [12—14]. In the course of reaction of furfuryl alcohol and benzyl alcohol on metal catalysts, SULTANOV and his coworkers [15] isolated aldehydes and hydrocarbons.

In the present investigation experiments were carried out to study the oxidative decarboxylation of furfuryl alcohol and benzyl alcohol in the reactor shown in [4]. For the experiments the reactor was filled with lead oxide catalyst and the temperature was 300 °C. By a charging pump furfuryl alcohol was bubbled through the foreheater — where it was vaporized — than the reactor filled with lead oxide. On the surface of the catalyst oxidative decarboxylation occurred. Isolation of the formed products was realized partly in coolers connected with the reactor, and partly in the absorption column and gasometer, respectively, joined to the coolers. Separation of the condensed products was carried out by fractionation and by

Table I
Percentage amount and physical constants of products formed during the oxidation of benzyl alcohol.
Experiments at different temperatures.

Reactor C°	B.p.	Amount %	n_D^{20}	C %	H %	Products
320—330	90	30	1,4989	92,02	7,52	benzene
320—330	110—115	25	1,4969	91,00	8,54	toluene
320—330	112—114	15	1,5459	79,08	6,18	benzaldehyde
300—310	—90	10	1,4985	91,83	7,60	benzene
300—310	111—114	35	1,4968	91,42	8,75	toluene
300—310	110—114	28	1,5446	79,83	6,49	benzaldehyde
Physical Constans						
benzene	80,1		1,5014	92,3	7,68	
toluene	110,8		1,4978	91,24	8,76	
benzaldehyde	179,5		1,5463	82,42	5,87	

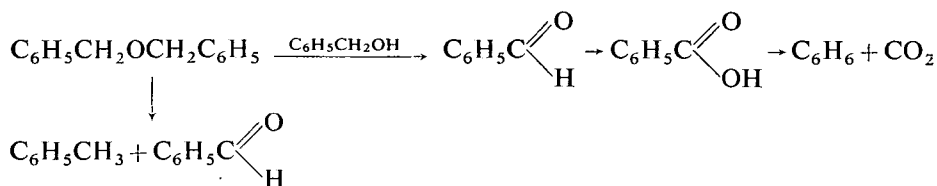
steam desorption of the absorbed products steam.

Study of the oxidative decarboxylation of furfuryl alcohol on lead oxide showed that furane, water and carbon dioxide were formed. Water and unchanged furfuryl alcohol were condensed in the coolers. Furane and carbon dioxide moved in the absorption column and gasometer, respectively. After steam desorption the furane vapors were condensed at -15°C .

The first step of the reaction is the oxidation of furfuryl alcohol into furfurool. At a considerable rate furfurool can be isolated. The formed furfurool is further transformed according to the known mechanism. Simultaneously with the oxidative decarboxylation pirophorous lead is formed.

Benzyl alcohol was oxidized at a temperature ranging from 300—310 and 320—330 $^{\circ}\text{C}$. From the separation of the condensed products it was established that at both temperatures the isolated organic phases contained benzene, toluene, benzaldehyde and unchanged benzyl alcohol, while water formed in the course of the reaction in a separate phase. It was further experienced that on raising the temperature the relative amount of toluene and benzaldehyde decreased and the quantity of benzene increased. The supposed mechanism of the reaction involves the formation of benzene in a way similar to the furfuryl alcohol — furane transformation. This is supported by the fact that from the reaction products we have succeeded in isolating

benzaldehyde which may be considered the first product of the oxidation. Chemical reactions are shown by the following scheme.



Quantitative data and physical constants of products formed at different temperatures are shown in Table I. It can be seen in the Table that the amount of toluene is considerable and its formation is the main direction of the reaction at lower temperatures. For the interpretation of the reaction mechanism it is reasonable to suppose that lead oxide, in the first step of the reaction catalyzes the formation of dibenzyl ether in a similar way as aluminium oxide does. On the surface of electrophilic lead oxide toluene and benzaldehyde are formed from dibenzyl ether, likely by a thermal disproportionation of ionic mechanism. As a final result, toluene is formed during the cleavage of an intermediate resulting from intermolecular anionotropy.

It may also be supposed that in the presence of pirophorous lead there is a reductive cleavage of dibenzyl ether to give toluene. This supposition has to be experimentally proved, since it has not been studied so far whether the hydrogenolysis can be catalyzed by pirophorous lead under the given experimental conditions.

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ГЕТЕРОГЕННОЕ КАТАЛИТИЧЕСКОЕ ОКИСЛЕНИЕ
ФУРФУРИЛОВОГО И БЕНЗИЛОВОГО АЛКОГОЛЕЙ
В РЕАКТОРЕ НАПОЛНЕННОМ ОКСИДОМ СВИНЦА

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Авторами изучалось окислительное декарбоксилирование фурфурилового и бензилового алкоholes в присутствии окиси свинца. Установлено, что в окислительном декарбоксилировании фурфурилового алкоholes получаются фуран и пиррофорный свинец. В окислительном декарбоксилировании бензилового алкоholes при различных температурах бензол, альдегид бензола и толуол были изолированы. Увеличивая температуру получается больше бензола и меньше толуола.