INVESTIGATIONS IN THE FIELD OF ETHERS. II

Study on the oxidation-reduction transformation of benzyl alcohol and dibenzyl ether in vapour-phase

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One of the purposes of this communication is to give a review of the literature on the oxidation-reduction transformations of benzyl alcohol, dibenzyl ether as well as of compounds of similar structure. Further, experimental studies have been carried out on dehydration and intermolecular dehydro-hydrogenation of benzyl alcohol in the presence of γ-aluminum oxide. Intramolecular oxidation-reduction of dibenzyl ether on γ-aluminum oxide and its thermal decomposition on quartz surface have also been carried out.

In the field of organic chemistry there are several transformations in which the hydrogen rearranges (disproportionates) intramolecularly or intermolecularly. Oxidation-reduction, dehydro-hydrogenizing processes of this kind are classified in the literature as follows:

1. In case of intramolecular processes the migration of hydrogen takes place within one molecule.

2. The other type of hydrogen rearrangement is intermolecular dehydro-hydrogenation, at which the rearrangement of hydrogen occurs among the molecules of the same substances. In the Soviet literature this reaction is termed irreversible catalysis.

3. Dehydro-hydrogenation may take place among various substances too.

In the field of hydrogen-rearrangements we have studied the dehydro-hydrogenation processes of cyclic ethers on the surface of metal catalysts in a continuous system by means of a vapour-phase heterogenous catalytic method (1, 2, 3). The cyclic ethers — independent of the number of carbon atoms of the ring — can be isomerized to carbonyl compounds. As to the oxidation state of the carbon atoms, playing a role in this process, one of the two atoms of first oxidation grade becomes zero and the other raises to a second oxidation grade in the course of the isomerization:
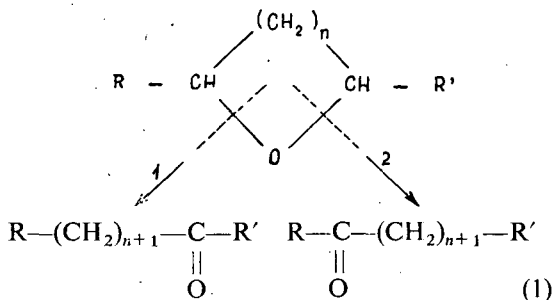

where:

n: 0, 1, 2, 3
R: H, alkyl
R′: H, alkyl, cycloalkyl, aryl.

(1)

In connection with our studies concerning the intramolecular dehydro-hydrogenation, we started an investigation on open-chained ethers. First of all we examined the oxidation-reduction transformation of dibenzyl ether, which under proper conditions disproportionates into toluene and benzaldehyde:

$$C_6H_5{-}CH_2{-}O{-}CH_2{-}C_6H_5 \longrightarrow C_6H_5CH_3 + C_6H_5CHO \qquad (2)$$
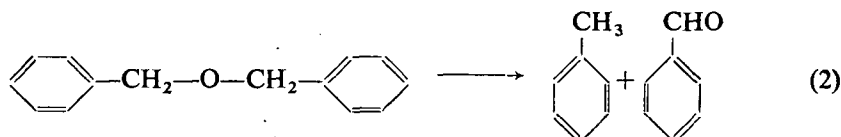
Further we have studied the direction of thermal decomposition of dibenzyl ether on the surface of quartz as well as on that of γ-aluminum oxide.

Simultaneously we carried out experiments on the dehydration and intermolecular dehydro-hydrogenation of benzyl alcohol taking place on γ-aluminum-oxide. The product of the dehydration of benzyl alcohol at 270° C was dibenzyl ether:

$$2\,C_6H_5{-}CH_2{-}OH \xrightarrow[\substack{270°C \\ -H_2O}]{\gamma-Al_2O_3} C_6H_5{-}CH_2{-}O{-}CH_2{-}C_6H_5 \qquad (3)$$
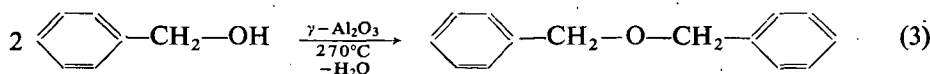
Under the same conditions but working at higher temperature toluene and benzaldehyde were formed:

$$2\,C_6H_5{-}CH_2{-}OH \xrightarrow[>300°C]{\gamma-Al_2O_3} C_6H_5CH_3 + C_6H_5CHO \qquad (4)$$
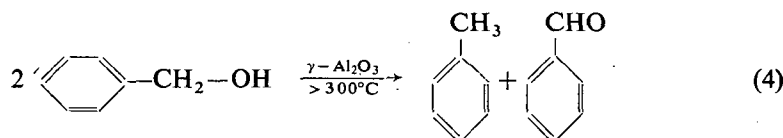
For the dehydration in heterogeneous phase various metal oxides, above all aluminum oxides, thorium oxides and tungsten pentoxides are suitable. These catalysts are very active between 300—360° C, but in their presence some dehydrations may take place at 230—250° C.

For the transformation of benzyl alcohol and dibenzyl ether on γ-aluminum oxide or on other dehydrating catalysts, very few references are given in the literature. The heterogenous catalytic dehydration of benzyl alcohol in vapour phase was first studied by SABATIER et al. (4,5). They carried out experiments on various dehydrating catalysts (Al_2O_3, TiO_2, etc.) but in every case some resin like product having indefinite structure was obtained. TETERIN (6) has studied the dehydration of benzyl alcohol on activated clay and observed the formation of dibenzyl ether only in the presence of p-amino-benzol-sulphonic acid. Later ADKINS and FOLKERS [7] examined the transformation of benzyl alcohol and dibenzyl ether at 340° C on aluminum oxide. In these case dibenzyl ether, toluene and benzaldehyde was in the product. In our Institute, experiments have been made on the transformation of benzyl alcohol on γ-aluminum oxide (8). We examined the formation of dibenzyl ether in a continuous system as a function of temperature and space velocity of benzyl alcohol.

From our point of view, it seems, important to pass in review the literature

according to the above account of the intra-, and intermolecular hydrogen rearrangement of benzyl alcohol, dibenzyl ether and of compounds with similar structure.

ZELINSKIJ and GLINKA (9, 10) have first studied the intermolecular dehydrohydrogenation, and it was ZELINSKIJ who termed the intermolecular hydrogen rearrangement as irreversible catalytic process. The investigations of these processes were carried out in a very wide range. A number of papers have been published on the irreversible catalysis in the group of hydrocarbons. According to ZELINSKIJ some of the molecules dehydrogenate, while the hydrogen formed in this process hydrogenates the other molecules. ZELINSKIJ et al. carried out investigations in the field of hydrocarbons, in particular with platinum, palladium and nickel catalysts.

In the field of hydrocarbons, some literary data regarding the irreversible catalytic processes performed on γ-aluminum oxide (11) occuring at 300° C are available. The reaction mechanism, however, cannot be applied for the dehydrohydrogenation of alcohol, since in this case the dehydration is the main process.

At the oxidation-reduction transformations mentioned above, any organic molecule being rich in hydrogen may act as hydrogen donor. Such are cyclohexane and its homologues, further the condensed hydrogenated aromatic rings, or compounds containing hydrogenated heterocyclic ring or active hydrogen atoms, e. g. primary or secondary alcohols. Benzyl alcohol may also act as a hydrogen donor (12). The Schiff basis containing azometine groups can be hydrogenated with benzyl alcohol. Likewise benzyl phenylethylamine can be prepared from β-phenylethylamine and benzyl alcohol in xylene solution with palladium catalyst.

The decomposition of dibenzyl ether was studied by CANNIZZARO, LOWE and ODDO (13—15). According to LOWE the optimum temperature of the decomposition is 295—298° C. Subsequent investigations were carried out by LACHMAN (16) who studied the thermal decomposition of benzyl alcohol and dibenzyl ether. At 210—215° C freshly distilled benzyl alcohol was heated in a sealed tube for 5 days, and water, dibenzyl ether, toluene, benzaldehyde and a high boiling substance were formed. He suggested that the formation of the last three substances was due to the decomposition of dibenzyl ether formed. He heated dibenzyl ether under similar conditions in a sealed tube, and the aforementioned products, were formed. The structure of this substance, however has not been elucidated. LACHMAN suggested that it was formed from dibenzyl ether and was not the product of the condensation of benzaldehyde.

SCHORIGIN (17) studied the rearrangement of benzyl ether in the presence of sodium metal. He obtained toluene and benzyl alcohol from dibenzyl ether. INGOLD (18) delt in his paper with the pyrolysis of dibenzyl ether carried out at high temperature. MASTAGLI et al. (19) have studied the dehydro-hidrogenation of benzyl alcohol and dibenzyl ether on cation exchanger of formaldehyde phenolsulphonic acid type. At 150° C they obtained dibenzyl ether by dehydration of benzyl alcohol. At 270—290° C toluene and benzaldehyde were formed. Under the latter conditions the same products were formed from dibenzyl ether. For the disproportionation of benzyl alcohol they suggested the following mechanism: At the first step ether was formed from two alcohol molecules and this reaction was followed by the conversion of ether to carbonyl compounds and hydrocarbons. DUCASSE (20) studied the pyrolysis of substituted benzyl ethers. On heating, benzyl ethers underwent an intramolecular dehydro-hydrogenation resulting in the formation of aldehyde and hydrocarbon:

$$\text{(5)}$$
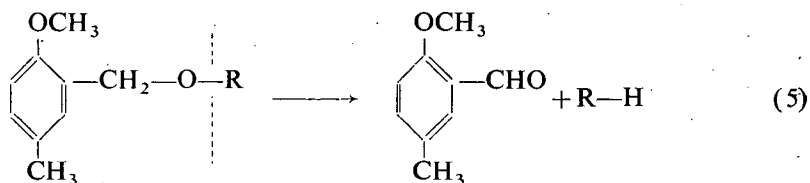
In the case dibenzyl ethers, the decomposition occured in both possible directions:

$$\text{(6)}$$
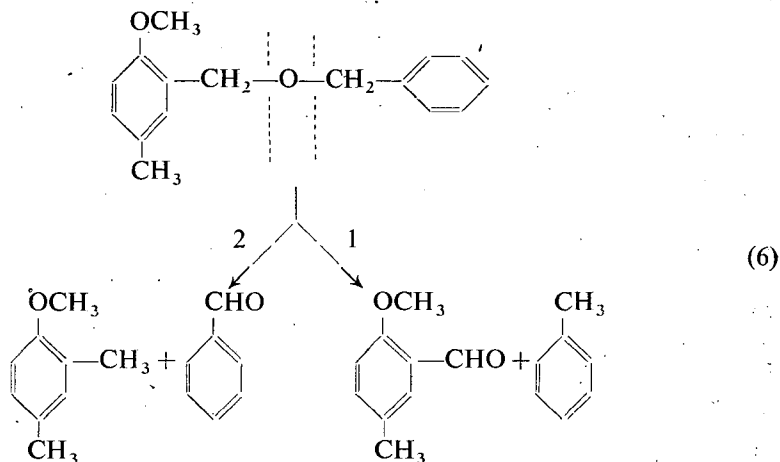
Reaction (1) was twice as fast as reaction (2). DUCASSE studied these pyrolytic processes by distilling the substances under atmospheric pressure. A similar phenomenon was found with α-naphtyl alcohol as well (21).
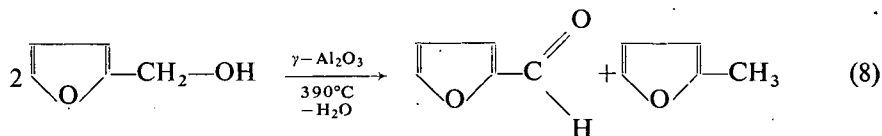
We have found some references in the literature on the heterogenous catalytic dehydro-hydrogenation of benzyl alcohol in vapour phase. SABATIER and SENDERENS (22) have made observations regarding the intermolecular oxidation-reduction of benzyl alcohol on reduced copper catalyst. At 300° C benzyl alcohol was converted into benzaldehyde. At 380° C they observed the formation of toluene, benzene, carbondioxide and hydrogen. Carbondioxide and hydrogen were formed from the reaction of water and carbon monoxide produced by the decarbonylation of benzaldehyde. These process was studied by ADKINS and FOLKERS (7) on aluminum oxide. The intermolecular dehydro-hydrogenations of some primary alcohols such as allylalcohol and furfuryl alcohol are similar to that of benzyl alcohol. The supposed reason of this phenomenon must be the conjugation of π-electrons with $C-OH$ bond.

KRETINSKY and NIKITINE (23) conducted allylalcohol through the aluminum oxide catalyst. The disproportionation resulted in propene and acroleine:

$$2CH_2 = CH - CH_2OH \rightarrow CH_2 = CH - CH_3 + CH_2 = CH - CHO \qquad (7)$$
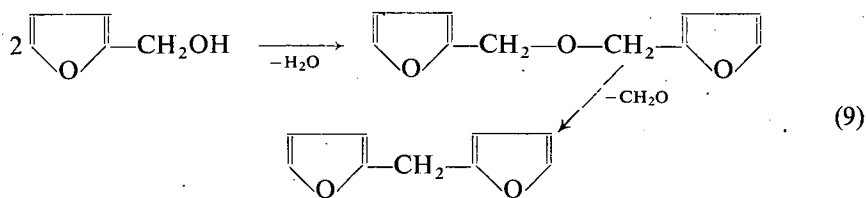
Several publications are dealing with heterogenous catalytic dehydro-hydrogenation of furfuryl alcohol in vapour-phase.

PAUL (24, 25) studied the oxidation-reduction of furfuryl alcohol at 390° C on aluminum oxide catalyst. The transformation resulted in water, furfural and methyl-furane:

$$2\ \text{[furan]}-CH_2-OH \xrightarrow[\substack{390°C \\ -H_2O}]{\gamma-Al_2O_3} \text{[furan]}-C{\overset{O}{\underset{H}{\diagup}}} + \text{[furan]}-CH_3 \qquad (8)$$

PAUL examined this process at 150° C on Raney-nickel catalyst (26, 27), and the formation of a considerable amount of furane besides furfural and methylfurane was observed. He suggested that furfuryl alcohol dehydrogenated on Raney-nickel and on the effect of hydrogen thus deliberated α-methylfurane was formed. The investigations of SHUJKIN and BEL'SKIJ (28—30) do not support these suggestions. In their works on the hydrogenation of α-furyl carbinoles they pointed out that α-furyl-carbinoles hydrogenated in the presence of nickel-aluminum alloyed catalyst resulting in α-tetrahydrofurfuryl-carbinoles. The Pd-carbon catalyst, however, had a selective effect and by the splitting of the C—OH bond it lead to the formation of α-alkyl-furane derivates. SULTANOV et al. (31) have studied the hydrogenation and dehydro-hydrogenation of benzyl- and furfuryl-alcohol on Cu-Zn-Al alloy catalyst. The dehydro-hydrogenating conversion yielded aldehyde and hydrocarbon beside a small amount of unconverted alcóhol. Hydrocarbon is the product of hydrogenation of aldehyde formed by the dehydrogenation. The conversion of furfuryl-alcohol to furfural and α-methyl-furane at 225—250° C is slower than that of benzyl alcohol to benzaldehyde and toluene. In their opinion the hydrogenation of benzaldehyd to toluene through alcohol is not excluded. SULTANOV et al. claim that such mechanism is possible when working with carrier metalcatalysts. The carriers are generally well dehydrating substances. Catalysts with good dehydrating ability have dehydrogenating activity too (32) at higher temperature. As the hydrogenation on such catalysts occurs at relatively higher temperature, the hydroxyl groups of the alcohols may be exchanged to hydrogens, in contradiction to the metal catalysts without carrier working at about 200°C. In IPATIEV's opinion the hydrogenation of benzaldehyde to toluene on iron surface takes place through benzyl alcohol (33). In relation with furfuryl alcohol we would mention another literary date. DINELLI et al. (34) have studied the dehydration of furfuryl álcohol in the presence of acidic catalysts. At the first step difurfuryl ether was formed as a result of an intermolecular dehydration, which in the second step converted with the splitting of formaldehyde to di-α-furfuryl methane:

$$2\ \text{[furan]}-CH_2OH \xrightarrow{-H_2O} \text{[furan]}-CH_2-O-CH_2-\text{[furan]} \xrightarrow{-CH_2O}$$

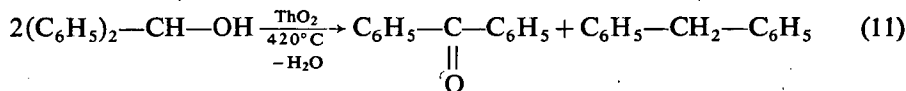$$\text{[furan]}-CH_2-\text{[furan]} \qquad (9)$$

A number of references are given in the literature on the dehydration and oxidation-reduction of secundary alcohols. Dibenzhydryl ether formed from di-

phenylcarbinol on thorium dioxide catalyst (5, 35):

$$2(C_6H_5)_2-CH-OH \xrightarrow[-H_2O]{ThO_2} (C_6H_5)_2-CH-O-CH-(C_6H_5)_2 \qquad (10)$$
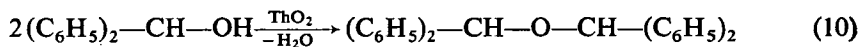
At 420° C diphenylcarbinole is disproportionated into diphenylmethane and benzophenone, moreover tetraphenylmethane is being formed (36):

$$2(C_6H_5)_2-CH-OH \xrightarrow[-H_2O]{ThO_2 \atop 420°C} C_6H_5-\underset{\underset{O}{\|}}{C}-C_6H_5 + C_6H_5-CH_2-C_6H_5 \qquad (11)$$

LACHMAN, — with intramolecular dehydro-hydrogenation (15) — obtained carbonyl compounds and hydrocarbone by distilling dibenzhydryl:

$$(C_6H_5)_2-CH-O-CH-(C_6H_5)_2 \rightarrow C_6H_5-\underset{\underset{O}{\|}}{C}-C_6H_5 + C_6H_5-CH_2-C_6H_5$$

$$(12).$$
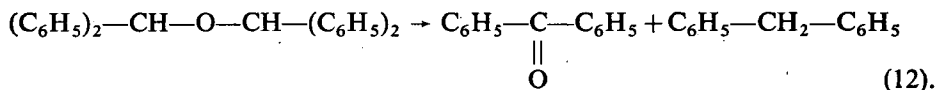
The intermolecular dehydro-hydrogenation of xanthydrol was studied by MEYER and SAUL (37) and naphtopyranol by FOSSE (38). On the basis of earlier data and of his own investigations, PAUL (24) set up a homologous series for the intermolecular oxidation-reduction, which, however, at present cannot be coordinated. At that time the oxidation-reduction transformation of benzyl alcohol on dehydrating catalysts was still unknown, as SABATIER's experiments (4,5) had yielded resin like product. This fact agreed with the erroneous supposition of GILMAN (39, 40) regarding the super aromatic character of furane compounds. According to this supposition PAUL set up the following series:

naphtopyranol > xanthydrol > benzhydrol > allyl alcohol > furfuryl alcohol > > benzyl alcohol.
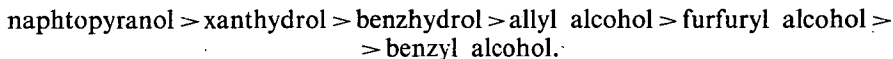
The diisochromanyl ether is also disproportionated by acids (41). The intermolecular oxidation-reduction was observed at α-furyl alkylcarbinoles too. These transformations were first studied by PAUL (25). At the transformation of such alcohols on γ-aluminum oxide catalyst the main reaction is not the intermolecular dehydrohydrogenation but the intramolecular dehydration:

$$(13)$$
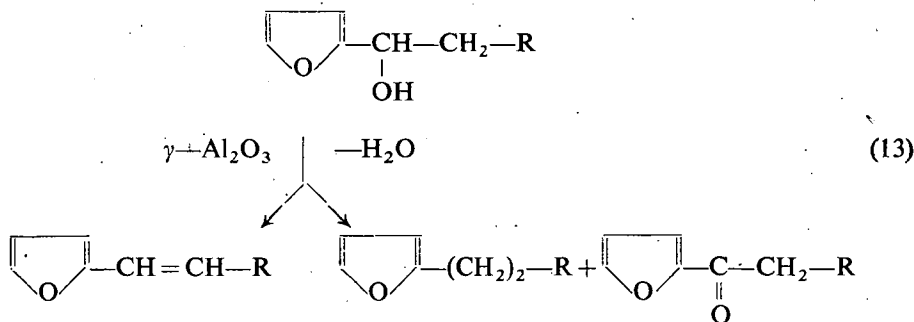
The ketone, thus formed, is able to transform, consequently it cannot be obtained in larger amount. SHUJKIN and BEL'SKIJ (42—44) while preparing α-alkenyl furanes

Table I.

	Substance conducted through the reactor	Charge of the reactor	Temperature °C	Dosing ml/hr	Space velocity hr^{-1}	Percentage of the substances in the product					
						Benzene	Toluene	Benz-aldehyde	Benzyl alcohol	Dibenzyl ether	High boiling point sub-stance
1.	Benzyl alcohol	$\gamma - Al_2O_3$	200	10	0,2	—	—	—	85	10	M
2.	Benzyl alcohol	$\gamma - Al_2O_3$	220	10	0,2	—	—	—	55	40	M
3.	Benzyl alcohol	$\gamma - Al_2O_3$	230	10	0,2	—	—	—	48	50	M
4.	Benzyl alcohol	$\gamma - Al_2O_3$	250	10	0,2	—	—	—	40	58	M
5.	Benzyl alcohol	$\gamma - Al_2O_3$	270	10	0,2	—	—	—	33	65	M
6.	Benzyl alcohol	$\gamma - Al_2O_3$	300	10	0,2	—	15	13	20	50	M
7.	Benzyl alcohol	$\gamma - Al_2O_3$	350	10	0,2	—	35	32	—	20	10
8.	Benzyl alcohol	$\gamma - Al_2O_3$	400	10	0,2	—	40	40	—	—	15
9.	Benzyl alcohol	$\gamma - Al_2O_3$	500	10	0,2	38	43	—	—	—	20
10.	Dibenzyl ether	$\gamma - Al_2O_3$	300	5	0,1	—	30	30	—	40	—
11.	Dibenzyl ether	$\gamma - Al_2O_3$	300	10	0,2	—	25	23	—	50	—
12.	Dibenzyl ether	$\gamma - Al_2O_3$	350	5	0,1	—	45	35	—	10	10
13.	Dibenzyl ether	$\gamma - Al_2O_3$	350	10	0,2	—	35	30	—	25	10
14.	Dibenzyl ether	$\gamma - Al_2O_3$	400	10	0,2	—	40	40	—	—	20
15.	Dibenzyl ether	$\gamma - Al_2O_3$	400	20	0,4	M	40	40	—	—	20
16.	Dibenzyl ether	$\gamma - Al_2O_3$	500	10	0,2	40	40	—	—	—	20
17.	Benzyl alcohol	$\gamma - Al_2O_3$	400	10	0,2	—	45	40	—	—	15
18.	Benzaldehyde	$\gamma - Al_2O_3$	400	15	0,3	—	—	100	—	—	—
19.	Benzaldehyde	$\gamma - Al_2O_3$	500	15	0,3	45	15	35	—	—	M
20.	Benzoic acid	$\gamma - Al_2O_3$	500	2,5*	—	100	—	—	—	—	—
21.	Benzene+Toluene(1:1)	$\gamma - Al_2O_3$	400	10	0,2	50	50	—	—	—	—
22.	Dibenzyl ether	quartz	400	10	0,2	—	M	M	—	95	—
23.	Dibenzyl ether	quartz	450	10	0,2	—	M	M	—	95	—
24.	Dibenzyl ether	quartz	500	10	0,2	—	12	10	—	76	—
25.	Dibenzyl ether	quartz	600	10	0,2	20	35	15	—	10	20

* g/hr   M: minimum

with a yield of 65—75% obtained 15—20% α-alkyl-furanes too. They did not examine the high boiling residue wich was formed with a yield of 20%. On the basis of these observations it was concluded that α-furyl-alkylcarbinoles are forming in the presence of aluminum oxide catalysts as a result of the intermolecular dehydro-hydrogenation, but the main direction of the transformation was the intramolecular dehydration.

In this publication we are accounting on such experimental results which were obtained while studying the intermolecular dehydration, intermolecular dehydro-hydrogenation of benzyl alcohol as well as the intramolecular dehydro-hydrogenation of dibenzyl ether.

The processes were studied in a continuous system on γ-aluminum oxide catalyst. The decomposition of dibenzyl ether was examined on the surface of quartz too. The amount of the products obtained by the reaction, was examined function of temperature. The temperature was varied between 200 and 600° C. The space velocity of the injected substances was not altered and on the basis of the previous experiment 0,2 hr^{-1} space velocity was the most suitable.

The experimental results are illustrated in tables (Table I.) and the $Y = f(t_v)$ functions (Fig. 1, 2, 3, 4) are shown in diagrams, where

Y: the yield of the formed product (%)
t: temperature (° C)
v: space velocity (hr^{-1}).

In each figure the curves symbolising the same substances are illustrated with the same line: benzyl alcohol: — ·· — ·· — ·· — dibenzyl ether: — — — — toluene: — — — — benzaldehyde: — · — · — benzene: — ··· — ··· — high boiling point substance: — — · — — · — — .

Evaluating the experiments we may draw the following conclusions:

Fig. 1. illustrates the amount of products, formed from benzyl alcohol on aluminum oxide catalyst, in function of temperature. At lower temperature dibenzyl ether was formed as a result of the intermolecular dehydration of benzyl alcohol:

$$2C_6H_5{-}CH_2{-}OH \xrightarrow[\substack{\gamma-Al_2O_3 \\ -H_2O}]{220-230°C} C_6H_5{-}CH_2{-}O{-}CH_2{-}C_6H_5 \qquad (14)$$
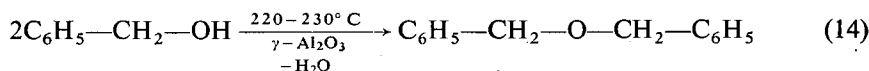
Under 200° C benzyl alcohol has not transformed at 0,2 hr^{-1} space velocity. It is obvious enough that the amount of benzyl alcohol decreases with rising temperature. The yield of dibenzyl ether varied with the temperature along a maximum curve. The maximum value was 65% at 270° C.

Raising the temperature, the yield of dibenzyl ether decreased and at 400° C it dropped to 0%. The rise of temperature favours the intermolecular dehydro-hydrogenation of benzyl alcohol:

$$2C_6H_5{-}CH_2{-}OH \xrightarrow[\substack{\gamma-Al_2O_3 \\ -H_2O}]{270°C} C_6H_5{-}CHO + C_6H_5{-}CH_3 \qquad (15)$$
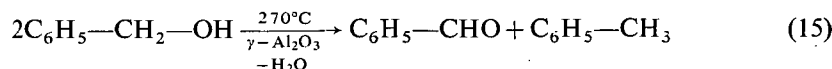
The formation of toluene and benzaldehyde began above 270° C and reached its maximum at 400° C. The amount of toluene varied along the saturation curve in function of temperature.
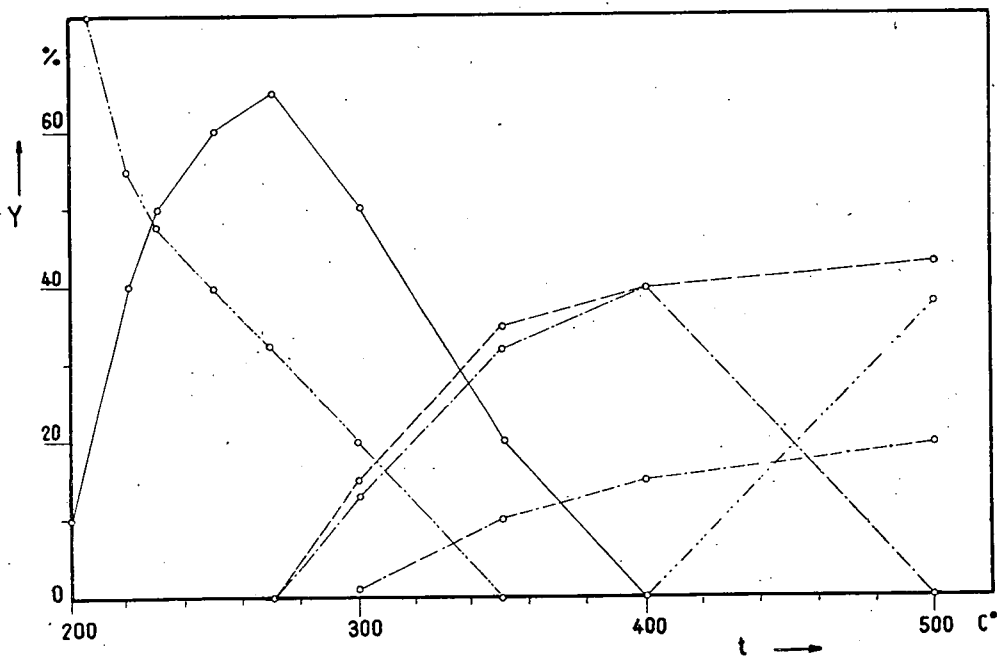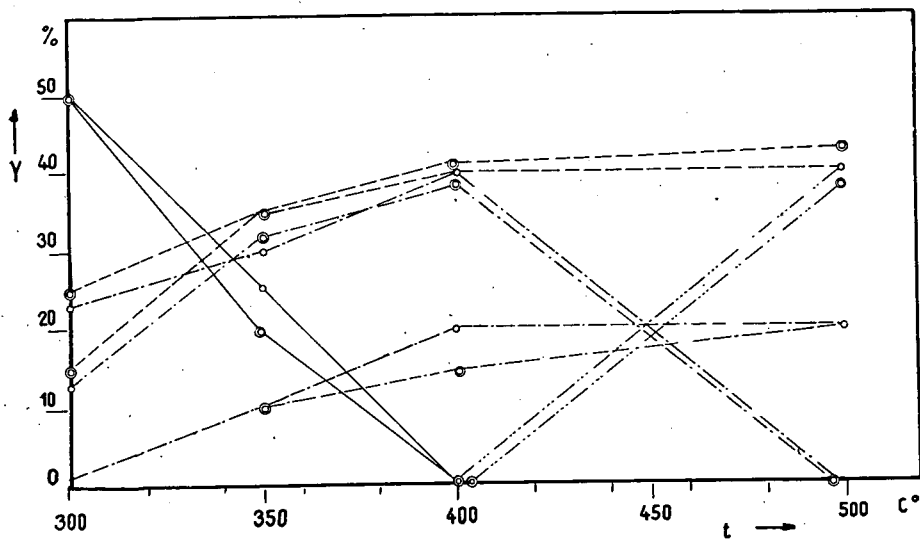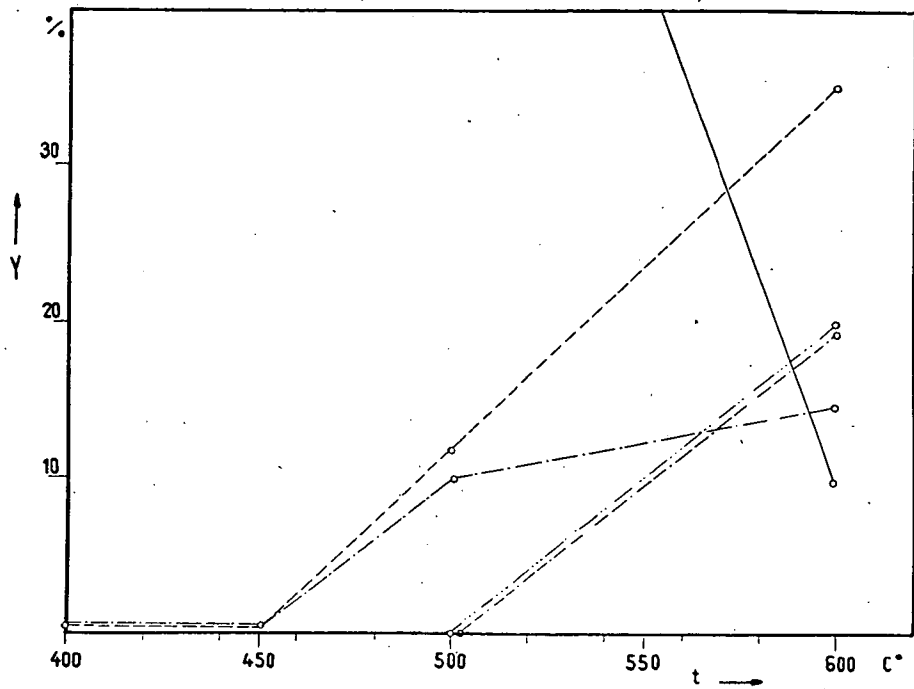
Fig. 1
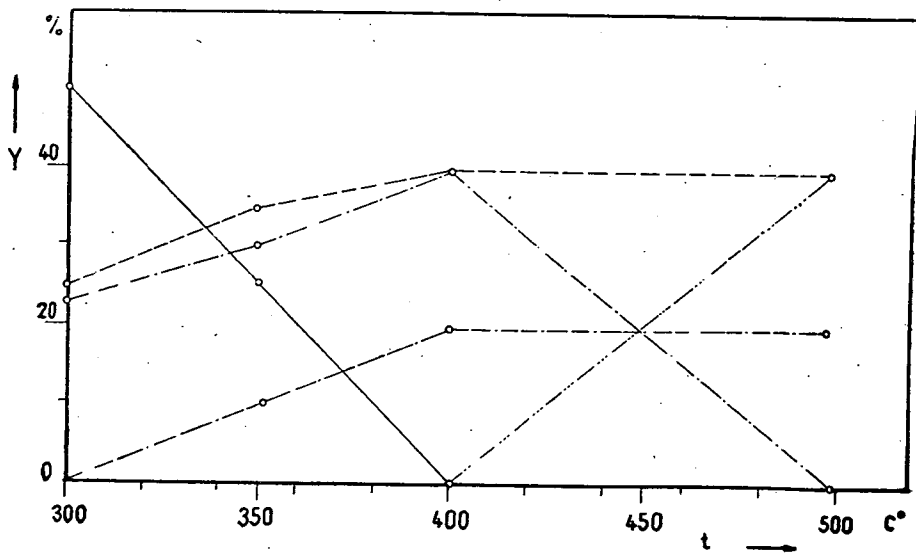

Fig. 2

Fig. 3

Fig. 4

In the case of benzaldehyde, it was not the saturation curve along which the variation occured. Namely the decarbonylation of benzaldehyde into benzene began at 400° C on aluminum oxide catalyst.

This transformation was proved by an experiment in which benzaldehyde was passed over aluminum oxide (see Table I., experiment 19.). The maximum yield of toluene and benzaldehyde was 40—45%. The curve of benzaldehyde ruled, in every case, under the curve of toluene.

We could observe in several other experiments (not shown in the table) that especially at small space velocity the amount of the low boiling fractions increased by 5—10% as compared to the amount of benzaldehyde. This may be due to the CANNIZZARO — oxidation-reduction as well as to the decarbonylation of benzaldehyde taking place on aluminum oxide catalyst.

We tried to prove the possibility of this phenomenon by studying the transformation of benzaldehyde and benzoic acid on this catalyst (Table I., experiment 19., 20.). No ether possible way may be presumed for the formation of toluene from benzaldehyde. CANNIZZARO reaction yielded benzyl alcohol which disproportionated into toluene and benzaldehyde. Benzoic acid conducted through the same catalyst at 500° C was completely decarboxylated. Above 300° C a high boiling substance formed, amounting to 20% at 500° C. Its melting point was between 130—190° C after several recrystallizations from ethanole. This wide boiling range indicated the presence of more than one substance. On the basis of its analysis its formula proved to be $C_{13-14}H_{10}$. The molecular weight of this aromatic hydrocarbon was between 150—170. As to its formation the conclusion may be drawn (34) that the mentioned product is the result of the dehydrogenation of diphenylmethane. It is reasonable to suppose that the substance in question was a mixture of methylene-diphenylenes ($C_{13}H_{10}$) and some antracene ($C_{14}H_{10}$). According to the literature the preparation of the latter compounds may be carried out from benzene and toluene on pumice (45). In Table I. the experiment 21. shows that substances with high boiling point have not formed on aluminum oxide. No further studies were made to elucidate the structure of the high boiling substances, for this problem had no influence on the main process i. e. on the dehydro-hydrogenation.

Fig. 2. shows the results of dibenzyl ether transformation on aluminum oxide catalyst. Dibenzyl ether decomposition was examined between 300—500° C. Above 300° C the formation of the same product was observed as in the case of benzyl alcohol. Intramolecular dehydro-hydrogenation was the first step of dibenzyl ether decomposition:

$$C_6H_5-CH_2-O-CH_2-C_6H_5 \xrightarrow[\gamma-Al_2O_3]{300°C} C_6H_5-CHO + C_6H_5-CH_3 \qquad (16)$$
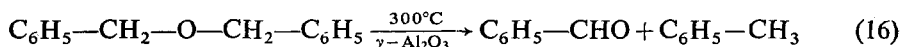
The secondary processes were corresponding to the transformation discussed in the casse of benzyl alcohol.

To conclude the catalytic effect of aluminum oxide catalyst on the decomposition of dibenzyl ether its thermal decomposition on quartz surface has been studied. This investigations are illustrated in Fig. 3. In case of 0,2 hr^{-1} space velocity the decomposition began merely above 450° C. At 500° C only 20% of dibenzyl ether was decomposed. The benzaldehyde decarbonylation began at 500° C, however, with considerably lower rate than observed on γ-aluminum oxide catalyst. At 600° C 15% benzaldehyde and 35% toluene were present. The amount of benzene was

20% at 600° C. The high boiling substance formed at the thermal decomposition on the quartz surface was not identical with that obtained in the presence of aluminum oxide catalyst.

Fig. 4. was constructed in order to elucidate the mechanism of the intermolecular dehydro-hydrogenation of benzyl alcohol. In this figure the oxidation-reduction of benzyl alcohol is seen together with the same reaction of dibenzyl ether. It is obvious to suppose that the dehydro-hydrogenation of benzylalcohol runs through dibenzyl ether in the presence of dehydrating catalyst. Comparing the corresponding curves (benzyl alcohol is marked - ●—●—●—●- and dibenzyl ether o—o—o—) we may conclude that the oxidation-reduction of benzyl alcohol runs through dibenzyl ether; in the first step dibenzyl ether is formed from benzyl alcohol, which at once decomposes to toluene and benzaldehyde by an intramolecular dehydro-hydrogenation at high temperature:

$$2C_6H_5-CH_2-OH \xrightarrow[-H_2O]{\gamma-Al_2O_3} C_6H_5-CH_2-O-CH_2-C_6H_5$$

$$C_6H_5-CHO + C_6H_5-CH_3 \tag{17}$$
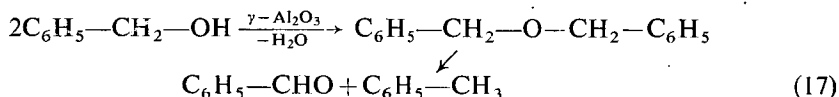
This processes may be compared with the transformation of alcohols and ethers into olefinic hydrocarbons. From ethylalcohol on aluminum oxide at lower temperature diethyl ether is formed, which is unstable at higher temperature. The direction of stabilization of the system tends towards the intramolecular dehydration leading to ethylene and water. The stabilization of dibenzyl ether, unstable at high temperature, may run only in the direction of intramolecular dehydrohydrogenation, since the formation of olefinic hydrocarbon and water is completely excluded in the case of systems having aromatic nucleus on the β and β' position.

As to the formation of ethylene, some workers suggested that the reaction ran through diethyl ether intermedier, while others supposed that ethylene and diethylether were formed independently by competitive reactions. BALANDIN et al. (46) have cleared the mechanism of this process using C^{14} isotope.

Fig. 5

Their investigations were performed on aluminum oxide at 300° C in a continous system. A mixture of ethanol and C^{14} labelled diethyl ether was passed over the catalyst. Studying the kinetics of the process, they observed that the rate of formation of ethylene from alcohol or from ether is roughly the same. To elucidate the mechanism of the process we might as well draw similar conclusions by examining the dehydrohydrogenation of benzyl alcohol in the presence of C^{14} labelled dibenzyl ether.
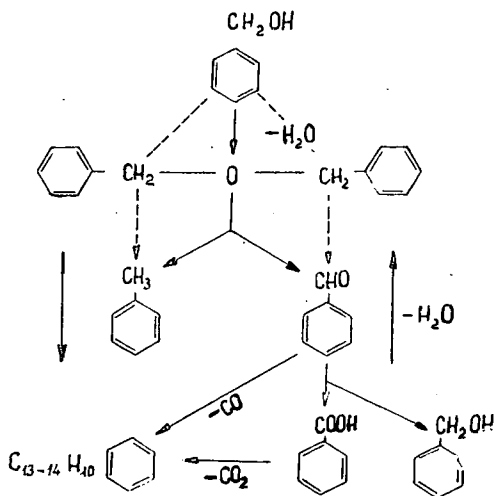
The elucidate the dehydration effect of aluminum oxide, new investigations have been started, the results of wich will probably lead to more exact knowledge of the mechanism of the reactions in question (47).

In fig. 5. the transformations of benzyl alcohol and dibenzyl ether, observed on aluminum oxide, have been summarized.

Experimental

We concerned ourselves with the starting substances in our previous publication (8). The physical constants playing a role in the process are summarized in table II.

Table II.

	Substance	B. p. °C	d gr/cm^3	n_D^{20}
1.	Benzyl alcohol	205	$1,050\frac{15}{15}$	1,5396
2.	Benzene	80	$0,8790\frac{20}{4}$	1,5011
3.	Toluene	110—111	$0,8669\frac{20}{4}$	1,4969
4.	Benzaldehyde	179—180	$1,0504\frac{15}{4}$	1,5455
5.	Dibenzyl ether	295—8	$1,0428\frac{20}{4}$	1,5614
6.	Benzoic acid	249	$1,2660\frac{15}{4}$	—

Description of the experiments

The process was studied at 200—600° C in a vertical supremaxglass tube reactor. The volume of the reaction space was 50 ml ($1,2^2 \cdot \pi \cdot 11 \sim 50$ ml). The temperature was measured on iron constantan thermoelement controlled by mercurial thermometer and regulated with a light resistant substance thermoregulator. (*Radelkisz, Budapest*). The sensitive point of the thermoelement was placed in a tube which was in the middle of the reaction space. The dosing was done with a syringe driven by a clockwork, thus securing the regular feeding of the reactors. At each experiment 50 ml substance was used and every experiment was repeated twice.

Examination of the raw products

The raw products gained as a result of the transformation were separated from water, dried and fractionated. The compounds were identified by microanalyses and determination of their physical constans.

Note

At the same time the catalytic and thermal decomposition of dibenzyl ether was also studied by RIECHE and SEEBOTH (48).

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ИССЛЕДОВАНИЕ ОКИСЛИТЕЛЬНО-ВОССТАНОВИТЕЛЬНЫХ ПРЕВРАЩЕНИЙ БЕНЗИЛОВОГО СПИРТА И ДИБЕНЗИЛОВОГО ЭФИРА В ПАРОВОЙ ФАЗЕ

М. Барток

В этой публикации даются с одной стороны, литературные просмотры в связи интермолекулярными и интрамолекулярными окислительно-восстановительными превращениями бензилового спирта, дибензилового эфира и им подобных веществ. С другой стороны, и экспериментально были исследованы дегидратация и интермолекулярная дегидро-гидрогенизация бензилового спирта, которые происходят на катализаторе γ·окиси алюминия. Было исследовано тоже интрамолекулярное оксидо-восстановление дибензилового эфира на поверхности γ·окиси алюминия и также его термический распад на поверхности кварца.

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