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Abstract

Full Text

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CATALYTIC DEHYDROGENATION OF ALKYLPHENOLS

Over the past 20-25 years ([1–3]), the preparation of alkylphenols and their derivatives with an unsaturated side chain has been described, as has their application in various branches of industry, especially in the production of various resins. The latter serve as good additives that improve their properties (for example, "korrezins"). Phenols with unsaturated side chains are obtained mainly by a synthetic method ([4]). In the scientific literature there are no data on the catalytic dehydrogenation of alkylphenols; it was therefore of interest to extend to these compounds our investigations on dehydrogenation ([5,6]). In the present study we have established that butyl- and isopropylphenols can readily undergo dehydrogenation while retaining the hydroxyl group of the phenol. From the standpoint of the multiplet theory, doublet reactions occur according to the schemes given below, in which the atoms reacting with the catalyst surface are enclosed in a frame:

[structural scheme of dehydrogenation of alkylphenols: an *o*-alkylphenol fragment with the reacting C—C ato

The results obtained are of definite interest and may find application in the synthetic-rubber, plastics, electrical-engineering, paint-and-varnish, and other industries.

Comparing the results of the dehydrogenation of butylphenol and isopropylphenol under approximately identical conditions (see tables), it is evident that butylphenol is dehydrogenated more readily than isopropylphenol. Hence it may be concluded that the reactivity of the alkylphenols undergoing dehydrogenation depends on their structure; the regularity noted by us in ([6]), namely that the rate of dehydrogenation and the yield increase with lengthening of the side chain in alkylbenzene, also extends to alkylphenols.

Experimental Part

Starting materials. Butylphenol and isopropylphenol were synthesized by the method of Tsukervanik and Nazarova ([2]). Butylphenol: b.p. 108–110°/6 mm, n_D^{20} 1.5181, d_4^{20} 0.9717, which corresponds, according to the literature data, to *o*-butylphenol ([2]). Isopropylphenol: b.p. 213–215°, n_D^{20} 1.5173, d_4^{20} 0.9730, which is close to the literature data ([2]) for *o*-isopropylphenol.

Determination of unsaturated compounds in the catalyzate. The amount of unsaturates in the catalyzate was determined bromometrically. Determination of unsaturates by the bromine method presents certain difficulties, since phenol itself and its alkyl derivatives brominate rather readily. Although numerous studies ([7]) have been devoted to the question of bromination of phenols and their derivatives, nevertheless, up to

not everything is yet clear in this reaction. Attention is drawn ([8]) to the need to take into account the influence of such factors as acid concentration, bromination time, bromination temperature, and excess bromine during bromination. Therefore, we first had to develop a method for analyzing phenols applicable to the investigation of our mixtures. The method of Rosenmund ([9]) was taken as the basis of the analytical procedure. We first tested this method on the starting alkylphenols. Bromination was carried out by us at room temperature with a 0.1 N bromine solution for 5 h. The bromine solution was always taken in excess. The percentage of unsaturated compounds in the catalyzate is calculated by the formula:

$$x = \frac{(a \cdot F_1 - bF_2)M}{P \cdot 100(2+4)},$$

where x is the molar percentage of the unsaturated compound in the mixture (in this case *o*-*n*-butenyl-2-phenol); M is the molecular weight of the unsaturated compound formed in the course of the reaction; P is the weighed portion of the substance under study; a and b are the numbers of milliliters of the bromine and hyposulfite solutions; F_1 and F_2 are their factors; 2 is the number of bromine atoms added at the double bond (in the side chain), and 4 is the number of bromine atoms absorbed by the ring.

Example: for the bromination of butylphenol, $a = 47.4$ ml of bromine solution with factor $F_1 = 0.9494$ was taken. For back titration, $b = 6.7$ ml of hyposulfite with factor $F_2 = 1.01$ was used; weighed portion $P = 0.152$ g. Substituting into the equation, we find $x = 62\%$.

Table 1

Dehydrogenation of butylphenol

Experiment No.	Substance passed	Experiment temperature, °C	Feed rate, h^{-1}	Diluent	Duration of experiment, min	Yield of catalyzate, wt.%	Conc. of unsaturated compound in catalyzate, wt.%
	Dehydrogenation of butylphenol						
1	Ethylbenzene	600	0.43	CO_2	60	–	52.6
2	Butylphenol	495	0.44	–	30	86.4	63.5
3	»	500	0.44	–	195	89.5	67.4
4	»	510	0.43	–	–	93.9	65.8
5	Ethylbenzene	600	0.35	CO_2	60	90.5	57.5
6	»	600	0.38	CO_2	60	–	32.6
7	Butylphenol	500	0.32	–	60	94.9	57.6
8	Ethylbenzene	600	0.40	CO_2	45	87.8	37.7
9	Butylphenol	500	0.43	CO_2	60	84.4	64.9
10	sec-Butylbenzene	530	0.50	–	30	76.3	42.4
11	Butylphenol	530	0.50	–	180	78.0	45.0
12	»	550	0.50	–	90	77.6	46.5
13	Ethylbenzene	600	0.58	CO_2	60	–	40.5
14	Butylphenol	505	0.48	–	45	91.9	43.8
15	»	535	0.40	–	30	89.5	53.9
16	»	535	0.40	CO_2	50	89.0	48.9
17	»	530	0.43	–	45	93.3	50.5
18	Ethylbenzene	600	0.64	CO_2	30	–	47.2
	Dehydrogenation of isopropylphenol						
19	Ethylbenzene	600	0.44	CO_2	–	95.4	38.2
20	Isopropylphenol	500	0.40	without CO_2	–	90.9	48.1
21	»	500	0.44	CO_2	–	95.0	51.7
22	Ethylbenzene	600	0.37	CO_2	–	–	44.3
23	Isopropylphenol	550	0.39	without CO_2	–	–	36.1

Experiment No.	Substance passed	Experiment temperature, °C	Feed rate, h^{-1}	Diluent	Duration of experiment, min	Yield of catalyzate, wt.%	Conc. of unsaturated compound in catalyzate, wt.%
24	»	500	0.40	without CO_2	–	–	35.5
25	»	525	0.60	without CO_2	–	–	36.3
26	Ethylbenzene	600	0.44	CO_2	–	–	46.3

For the dehydrogenation of alkylphenols, copper–chromium catalyst No. 4 was used. The experiments were carried out by the flow method with dilution by CO_2 and without dilution, at atmospheric pressure. The apparatus and procedure did not differ from those described in our previous works ([10], [11]). The tube was quartz; the thermocouple was in the catalyst bed.

The activity of the catalyst was determined by passing alkylbenzenes at 600° before and after experiments with an alkylphenol. The results of the experiments (see Table 1) show that the catalyst is not poisoned and does not decrease its activity after alkylphenols have been passed over it.

Dehydrogenation of butylphenol. The results of experiments on the dehydrogenation of butylphenol are given in Table 1, from which it is evident that butylphenol is readily dehydrogenated over a copper–chromium catalyst at lower temperatures than alkylbenzenes ([5], [6]), even in the absence of a diluent. The percentage of unsaturated compounds in the condensate is rather high. Analysis of the exit gases (see Table 2) shows that, in addition to dehydrogenation of butylphenol, cleavage of the side chain also occurs; the exit gases contain, besides hydrogen, methane, ethane, and ethylene.

Table 2

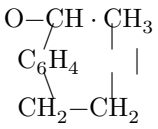
Gas analysis

Experiment No.	Experiment temp., °C	CO_2	C_2H_4	H_2	CH_4	C_2H_6	O_2	CO
14	505	0.0	6.4	33.6	39.6	19.7	0.0	0.0
15	535	0.0	9.2	24.1	42.2	21.9	0.6	0.0
16*	535	0.0	18.7	8.2	33.6	23.1	0.0	16.8
2	495	0.0	2.8	80.7	12.1	4.6	0.1	0.0

Experiment No.	Experiment temp., °C	CO_2	C_2H_4	H_2	CH_4	C_2H_6	O_2	CO
4	500	0.0	7.4	45.5	37.5	9.4	0.0	0.0

* Experiment 16 was carried out with dilution by CO_2; therefore the gas contains much CO.

The butenylphenol isolated from the condensate had b.p. 110–112°/5 mm, n_D^{20} 1.5384, d_4^{20} 0.9975. The resulting *o*-butenyl-2-phenol dissolves well in alcohol and in alkali. From *o*-butenyl-2-phenol, 2-methylchroman was obtained



by Claisen and Tietze ([12]). The 2-methylchroman obtained boiled at 220° (literature data 219.5–221° ([12])). This proves that the reaction product is *o*-butenyl-2-phenol; as regards the double bond,

Table 3

Passed substance	Experiment temp., °C	Catalyst yield, wt.%	n_D^{20}	Concentration of unsaturated compounds in the catalyst, wt.%
Copper-chromium catalyst				
Ethylbenzene	605	77.0	1.5235	55.0
Isopropylphenol	500	75.0	1.5295	43.4
»	»	73.5	—	46.9
Ethylbenzene	605	76.6	1.5165	42.0
Catalyst No. 40				
Ethylbenzene*	600	97.2	1.5195	47.0
Isopropylphenol	498	72.5	1.5240	45.5
o-Butylphenol	495	74.7	1.5250	58.5

* The experiment with ethylbenzene was carried out in the presence of water (1 : 2).

in the side chain, then under the influence of HBr it could migrate from the α- to the β-position.

Dehydrogenation of isopropylphenol. The experiments were carried out on a copper–chromium catalyst preliminarily reduced with hydrogen at 500°. The catalyst volume was 20 ml. The diluent was CO_2. The feed rate was 0.30 h^{-1}. The results of the experiments are given in Table 3.

The results of experiments on another sample of a less active copper–chromium catalyst are given in Table 1. The yields of isopropenylphenol at 500° are fairly high.

For the dehydrogenation reaction of alkylphenols, another oxide catalyst, No. 40 ([13]), was tested; it gave high yields of unsaturated compounds in the catalyzate. The results of the experiments are given in Table 3.

The analysis of the exit gases in the dehydrogenation of isopropylphenol and butylphenol is as follows:

H_2	CH_4	C_2H_4	C_2H_6	C_3H_6
79.2	11.85	5.3	–	3.64
68.8	16.3	6.0	4.3	4.3

Analysis of the gases shows that, also in the case of oxide catalyst No. 40, along with dehydrogenation, cleavage of the side chain takes place.

Thus, butyl- and isopropylphenols are dehydrogenated on copper–chromium catalyst No. 4 and on oxide catalyst No. 40 at atmospheric pressure, without diluent and with diluent, at 495–510°, with satisfactory yields of *o*- and *p*-butenyl-2-phenol and isopropenylphenol. The catalyst is not poisoned and does not lose its activity.

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