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Abstract

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STUDY OF THE THERMAL TRANSFORMATIONS OF PHENOL AT HIGH HYDROGEN PRESSURES

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Ipatiev and Orlov ([1]), as well as Kling and Florentin ([2], [3]), noted the high thermal stability of phenol at 500°. Only when the temperature was raised to 650-750° were thermal transformations of phenol observed; in the gaseous reaction products, the presence of hydrogen, methane, carbon monoxide, ethylene, acetylene, and butadiene was established ([4], [5]). Kouley ([6]) investigated the thermal transformations of phenol at 410, 430, and 450° in the absence of catalysts under hydrogen pressure. Under the conditions he studied (at an initial hydrogen pressure of 100 atm), phenol underwent only a very slight transformation with the formation of benzene, the yield of which at 450° (over 2 hours) amounted to only 1.8 wt.% of the initial phenol.

We carried out the study of the thermal transformations of phenol at high hydrogen pressures in a stainless-steel reactor of 120 ml capacity with a hydraulic seal. In each experiment, 40 g of phenol was charged into the reactor. The phenol had been preliminarily distilled on a rectification column with an efficiency of 25 theoretical plates; b.p. 181.8-182.0°/760. The initial hydrogen pressure in different experiments ranged from 100 to 300 atm. The temperature of the experiment was maintained constant within $±$2° for 3 hours. The working pressure in different experiments ranged from 260 to 680 atm. After completion of the experiment, the pressure was slowly reduced to atmospheric; the liquid products were collected in a trap under cooling. The reactor was then washed with ether, which was added to the discharged product and dried with anhydrous sodium sulfate.

The reaction products were fractionated on a rectification column with an efficiency of 25 theoretical plates; first the ether was distilled off, after which the following fractions were isolated: fraction I—b.p. 60-83°; fraction II—b.p. 83.1-175°; fraction III—b.p. 175.1-183°. Fraction I contained predominantly benzene; about 90% of it had b.p. 75-83°, n_D^{20} 1.4863-1.4918. As a result of repeated fractionation of fraction I from six experiments and subsequent chromatographic separation on silica gel, a cyclohexane fraction with n_D^{20} 1.4238 was isolated; the somewhat lowered value of n_D^{20} indicates the possible presence in this fraction also of methylcyclopentane and hexane. Fraction II (n_D^{20} 1.4948-1.4975) was intermediate (no flat sections were observed on the distillation curve). Fraction III contained unchanged phenol. The high-boiling residues (with b.p. above

183°) were studied separately.

Experiments carried out at 460° and an initial hydrogen pressure of 100 atm, in agreement with ([6]), showed that under these conditions the formation of benzene from phenol occurs to a very slight extent.

The results of experiments carried out at 490°, $\tau = 3$ hours, and at different initial hydrogen pressures are given in Table 1. From consideration of the data in this table it follows that, with an increase in the initial hydrogen pressure from 100 to 300 atm, the yield of the benzene fraction increases almost threefold.

Table 1

Thermal transformations of phenol at high hydrogen pressures ($t = 490°$, $\tau = 3$ hours)

Initial hydrogen pressure, atm	Working pressure, atm	Total yield of liquid products* (wt. % relative to charged phenol)	Fraction I 60–83°	Fraction II 83–175°	Fraction III 175–183°	Residue
100	260	92.3	8.2	2.3	66.0	15.8
100	275	93.0	8.9	3.4	64.2	16.5
200	425	84.8	15.3	3.4	50.0	16.1
200	435	84.4	16.4	3.6	48.5	15.9
300	680	80.9	24.6	4.1	40.2	12.0
300	675	77.4	22.2	3.2	42.8	9.2

* Without water.

As can be seen from Table 1, the discrepancies between the results of parallel experiments are small.

To determine the homogeneity of the process under study, experiments were carried out at 490°, an initial hydrogen pressure of 100 atm, and an experiment duration of 3 hours, with shavings of the same stainless steel added to the reactor. The surface area of the shavings was 550 cm^2; the internal surface area of the reactor was 330 cm^2. These experiments showed that the magnitude of the metal surface and its ratio to the reactor volume do not affect the reaction rate:

S, cm^2	330	880

S/v, cm^{-1}	2.75	7.2
Yield of fraction I, wt. % relative to charged phenol	8.5	8.8

Thus, the process under study is homogeneous.

The residues after distillation were combined and again distilled on a rectification column. The fraction with b.p. 183-185° (36 wt. %) was unchanged phenol; the fraction with b.p. 185.1-215° (18 wt. %) consisted to a considerable extent of *n*-cresol, which was identified in the form of *n*-cresoxyacetic acid, m.p. 135.5-136°. The residue after distillation on the column was distilled from a Claisen flask; fractions with b.p. 220-257 and 257-260° were obtained, as well as a solid residue in which, after removal of the higher phenols (soluble in alkali), the presence of diphenylene oxide was established, m.p. 81-82° (from methyl alcohol). According to literature data (7), m.p. 82.8°.

$C_{12}H_8O$.	Found, %:	C 85.75; H 4.90
	Calculated, %:	C 85.72; H 4.76

The fraction with b.p. 220-257° contained diphenyl, m.p. 69-70°; a mixed sample with pure diphenyl did not change the melting point. The fraction with b.p. 257-260°, judging from the analytical data, apparently contained tetrahydrodiphenylene oxide.

$C_{12}H_{12}O$.	Found, %:	C 83.54; 83.65; H 7.44; 7.45
	Calculated, %:	C 83.66; H 6.97

Table 2 gives data on the composition of the gaseous reaction products. The data of Table 2 (especially the last column) indicate a considerable acceleration of the process of thermal decomposition of phenol with increasing hydrogen pressure. The hydrocarbon composition of the gaseous reaction products in the pressure range studied shows no substantial changes.

Table 2

Composition of gaseous products in volume percent
(experiments carried out at 490°, $\tau = 3$ hours)

Initial hydrogen pressure, atm	H_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	CO	CO, mol. % relative to charged phenol
100	90.1	3.5	2.1	0.7	0.1	2.0	1.7

Initial hydrogen pressure, atm	H_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	CO	CO, mol. % relative to charged phenol
300	87.0	3.8	2.7	1.0	0.2	4.6	7.4

The primary stage of the thermal decomposition of phenol is apparently the rupture of the O–H bond with formation of the phenoxy radical (see (8)). Therefore, the presence of diphenyl ether could have been expected in the reaction products; however, we were unable to isolate the latter from the high-boiling fractions. We assumed that the diphenylene oxide we found could have formed from diphenyl ether. This assumption was confirmed by an experiment carried out with diphenyl ether (32 g) at 490°, $\tau = 3$ hours, and an initial hydrogen pressure of 200 atm. In the reaction products, along with unchanged diphenyl ether, 13.8 wt. % benzene and 14.3 wt. % phenol were found. Diphenylene oxide was isolated from the high-boiling residue (6.1 wt. %); a mixed sample with the diphenylene oxide obtained in the experiments with phenol (see above) did not change the melting point.

The investigation performed showed that thermal transformations of phenol at high hydrogen pressures lead to the formation of benzene as the main product. In the high-boiling reaction products the presence of *n*-cresol, diphenyl, and diphenylene oxide was established, as well as, apparently, tetrahydrodiphenylene oxide. The homogeneity of the process studied was proved, and it was found that the yield of benzene, as well as of gaseous reaction products, increases markedly with increasing hydrogen pressure.

Comparison of the literature data on the considerable thermal stability of phenol at 500° with the results of the present investigation makes it possible to conclude that the reaction studied proceeds by a radical-chain mechanism with the participation of hydrogen. The scheme of this mechanism may be represented as follows:

$$C_6H_5OH \rightarrow C_6H_5O\cdot + H\cdot \quad (1)$$

$$H\cdot + C_6H_5OH \rightarrow C_6H_5\cdot + H_2O \quad (2)$$

$$\rightarrow CO + \text{hydrocarbon radicals R} \quad (3)$$

$$C_6H_5\cdot + H_2 \rightarrow C_6H_6 + H\cdot \quad (4)$$

$$R + H_2 \rightarrow RH + H\cdot \quad (5)$$

$$2C_6H_5\cdot \rightarrow C_6H_5\cdot C_6H_5 \quad (6)$$

$$C_6H_5\cdot + C_6H_5O\cdot\text{leftarrows}(C_6H_5)_2O \rightarrow (C_6H_4)_2O + H_2 \quad (7)$$

diphenylene oxide

Reaction (1) is the primary stage of the thermal decomposition of phenol; the interaction of the atomic hydrogen formed in this reaction with a phenol molecule (reaction (2)) leads to detachment of the hydroxyl group from the benzene nucleus (similar to the dealkylation of alkylbenzenes (9)). This process is accelerated by hydrogen pressure, since the latter determines the rate of reaction (4) and analogous reactions (5) involving molecular hydrogen, which generate atomic hydrogen.

Our experiments showed that hydrogen pressure also accelerates the decomposition of phenol with formation of gaseous products. We assume that this process is likewise connected with the participation of atomic hydrogen, the addition of which to one of the carbon atoms of phenol leads to a decrease in the strength of the bond between this and the neighboring carbon atoms. Rupture of this bond

C—C, apparently, leads to the formation of an unstable biradical, which undergoes further decomposition into carbon monoxide and hydrocarbon radicals. The latter, in turn, are capable of alkylating phenol molecules with the formation, in particular, of *p*-cresol, which we detected in the reaction products.

As is evident from the proposed scheme, reactions (2)—(5) are chain-propagation processes, while reactions (6) and (7) are chain-termination processes; the higher the hydrogen pressure, the greater the length of the reaction chains. Thus, this scheme satisfactorily interprets the data we obtained on the composition of the products of the thermal transformations of phenol under high hydrogen pressure and on the effect of the magnitude of this pressure on the rates of the various stages of the process studied.

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