HOMOGENEOUS DESTRUCTIVE HYDROGENATION OF CRESOLS

AT HIGH PRESSURES OF HYDROGEN

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Fischer and Tropsch [1], in an investigation of the berginization of the three isomeric cresols at 460° at an initial hydrogen pressure of 95 atm, observed partial elimination of a methyl group with formation of phenol. Later, Hagemann and Neuhous [2] found that in the destructive hydrogenation of high-boiling phenols in presence of Fe₂O₃ or Al₂O₃ low-boiling phenols are formed. Cawley [3] (1933) investigated the homogeneous destructive hydrogenation of m-cresol (in absence of catalysts) at 500° at an initial hydrogen pressure of 100 atm for two hours. Under these conditions the author obtained 24% by weight of phenol, 21% by weight of aromatic hydrocarbons, and 6% by weight of water (on the amount of cresol taken). A paper by Kalechits and Salingareeva [4] gives data on the destructive hydrogenation of cresols at 478° at a hydrogen pressure of 370 atm in presence of an iron catalyst. The amounts of phenol obtained were about 12% from m-cresol, about 16% from o-cresol, and about 18% from p-cresol (the yields of neutral products were 33.7%, 37.5%, and 43.3%, respectively). While the present investigation was in progress, a paper was published by Ielinek [5], who carried out experiments in a flow apparatus at 600° under a hydrogen pressure of 70 atm (molar ratio of hydrogen to cresol of 1:1). In absence of catalyst the author obtained 17.6 moles percent of phenol, and in presence of silica gel as catalyst he obtained 28.0 moles percent of phenol (on the amount of p-cresol taken).

The present work, which forms a continuation of investigations on the homogeneous destructive hydrogenation of aromatic hydrocarbons and their derivatives [6, 7], had the object of studying the transformations of o-, m-, and p-cresols in absence of catalyst under high pressures of hydrogen.

EXPERIMENTAL

The experiments were carried out in a 120 ml stainless steel reactor having a hydraulic seal. In each experiment 40 g of the cresol under investigation was placed in the reactor. The cresols were first distilled through a column of 25-plate efficiency and then had the following constants: o-cresol, b. p. 191.3-191.5° (760 mm) and $n^{20}D$ 1.5454; m-cresol, b. p. 202.6-202.8° (760 mm) and $n^{20}D$ 1.5398; p-cresol, b. p. 202.2-202.4° (760 mm) and $n^{20}D$ 1.5394. Initial hydrogen pressures varied from 100 to 300 atm in the various experiments (the working pressures varied correspondingly from 260 to 650 atm). The reactor was heated to the required temperature over a period of 90 minutes, after which the temperature was kept constant within $\pm 2^{\circ}$ for three hours. When the reactor was cool, the pressure was gradually lowered to atmospheric; the liquid products were collected in a cooled trap. The reactor was then rinsed out with ether, and the ethereal solution and liquid products were combined and dried with anhydrous sodium sulfate. The liquid reaction products were fractionated through the 25-plate column; when the ether had been removed, we collected the following fractions: Fraction I, b. p. 60.0-95.0°; Fraction II, b. p. 95.0-113.0°; Fraction III, b. p. 113.0-175.0°; Fraction IV, b. p. 175.0-192.0°; * Fraction V, b. p. 192.0-203.0°.*

^{*}In the case of o-cresol: Fraction IV, b. p. 175.1-186.5°; Fraction V, b. p. 186.5-192.0°.

TABLE 1

Homogeneous Destructive Hydrogenation of Toluene and Phenol at 490° under Various Initial Pressures of Hydrogen for Three Hours

Initial hydrogen	Yield of benzene fraction (% by wt.)				
pressure (atm)	from toluene	from phenol			
100	19.2	8.9			
200	33.4	16.4			
300	46.0	24.6			

Fraction I consisted mainly of benzene; about 85% of this fraction had b. p. 75-95° $(n^{20}D 1.4812-1.4872)$. Refractionation of Fraction I followed by chromatographic separation on silica gel gave a cyclohexane fraction of $n^{20}D 1.4264$. Fraction II $(n^{20}D 1.4920-1.4960)$ contained toluene. Fraction III $(n^{20}D 1.4941-$ 1.4973) was an intermediate fraction. Fraction IV contained phenol and a little unchanged cresol. Fraction V was unchanged cresol containing a little phenol.

The high-boiling residues were investigated separately. The CO and CO_2 contents

of the gaseous products were determined; their hydrogen and hydrocarbon contents were determined by chromatographic separation. As well as carrying out the experiments on the homogeneous destructive hydrogenation of cresols, we investigated the behavior of phenol and toluene under the same conditions. This investigation had the object of comparing the rates of elimination of hydroxy and methyl groups from the benzene nucleus during homogeneous destructive hydrogenation. The substances used had the following constants: phenol, b. p. 181.8-182.0° (760 mm); toluene, b. p. 110.8°; $n^{20}D$ 1.4968. In each experiment 40 g of the substance was placed in the reactor. The experimental procedure was the same as for the cresols.* As the benzene fraction we took the fraction of b. p. 60-83° in the experiments with phenol and the fraction boiling up to 83° (start of boiling not below 77.5°) in the experiments with toluene.

<u>Comparison of the rates of the demethylation of toluene and dehydroxylation of phenol</u>. We carried out the experiments with phenol and toluene at 490° and at initial hydrogen pressures of 100, 200, and 300 atm. It follows from the results of these experiments (Table 1) that the elimination of the methyl group from toluene occurs about twice as fast as the dehydroxylation of phenol.

Table 1 shows that increase in hydrogen pressure considerably accelerates both of the processes studied. The results lead us to suppose that, under the conditions of homogeneous destructive hydrogenation, it is possible to effect the demethylation of cresols with yields of phenol exceeding the yields of toluene and benzene.

Effect of temperature on the homogeneous destructive hydrogenation of cresol. Table 2 gives the results of experiments with o-cresol at 460°, 475°, and 490° under an initial hydrogen pressure of 300 atm (duration of experiment, three hours).

Table 2 shows that, under the given conditions, the yield of the phenol fraction (Fraction IV) already attains 15.3% by weight on the original cresol (about 35% by weight or 40 moles percent on the cresol that reacted) at 460°. Rise in temperature to 475° and 490° leads to increase in the yield of phenol to 21.6 and 30.0% by weight, respectively, on the original cresol (38 and 33% by weight or 41 and 47 moles percent on the cresol that reacted). The over-all yield of benzene (Fraction I) and toluene (Fraction II) rises from 8.5% by weight on the original cresol at 460° to 27.2% by weight at 490° (19.3 to 30.0% by weight or 23.3 to 38.4 moles percent on the cresol that reacted). The results indicate the possibility of obtaining considerable yields of phenol in the homogeneous destructive hydrogenation of o-cresol. Further experiments with o-, m-, and p-cresols were carried out at 490°.

Effect of hydrogen pressure on the homogenous destructive hydrogenation of cresols. The results of experiments on the homogeneous destructive hydrogenation of o-, m-, and p-cresols at 490° are given in Table 3.

An examination of Table 3 enables us to draw the following conclusions: 1) in experiments with o-cresol the maximum yield of phenol (about 30% by weight on the original phenol) is already attained at an initial hydrogen pressure of 200 atm. Further increase results only in increased yields of benzene and toluene; 2) the homogeneous destructive hydrogenation of m-cresol is much slower than that of o-cresol. The yield of phenol is approximately doubled when the initial hydrogen pressure is increased from 100 to 300 atm. Over this range of pressures the over-all yield of benzene and toluene is more than doubled (almost trebled when calculated in moles percent); 3) at an initial hydrogen pressure of 100 atm the yield of phenol from p-cresol is somewhat less * In the experiments with toluene it was not necessary to rinse out the reactor with ether.

TABLE 2

	Yield of liquid products other than water (% by wt. on cresol take						
Temp . (°C)	in all	Fraction I 60-95°	Fraction I 95–113°	Frac. III 113—175°	Fraction IV, 175-186,5°	Fraction V 186,5—192	Residue
460 475 490	88,4 84,7 78,0	1,2 2,9 13,5	7,3 8,8 13,7	2,4 2,2 4,1	$ \begin{array}{r} 15,3\\ 21,6\\ 30,0 \end{array} $	$56,0 \\ 43,2 \\ 9,4$	6,2 6,0 7,3

Homogeneous Destructive Hydrogenation of o-Cresol at an Initial Hydrogen Pressure of 300 atm at Various Temperatures for Three Hours

than from o-cresol, but considerably greater than from m-cresol. When the pressure is raised from 200 to 300 atm there is scarcely any rise in the yield of phenol. There is a simultaneous rise in the yield of benzene and toluene, which, however, is much slower than in the case of o-cresol; 4) the over-all conversion of p-cresol at 300 atm (81.3%) is close to the conversion of o-cresol at 200 atm (79.9%). However, under these conditions the over-all yield of liquid products is considerably higher in the case of o-cresol. From this we may conclude that the observed side reaction of cleavage of the aromatic nucleus with formation of carbon monoxide and paraffins which occurs during the homogeneous destructive hydrogenation of phenols proceeds more vigorously with p-cresol than with o-cresol. This view was later confirmed by the analysis of the gaseous reaction products.

Investigation of the high-boiling reaction products. Fractionation residues from the experiments with o-cresol were combined and redistilled through a column. In the 201.5-202.4° (760 mm) fraction we identified p-cresol in the form of (p-tolyloxy)acetic acid, m. p. 135.5-136°. From the 209-215° (760 mm) fraction we isolated 2,5-xylenol in the form of (2,5-xylyloxy)acetic acid, m. p. 117-118°. In the 215-222.2° (760 mm) fraction we identified p-ethylphenol in the form of (p-ethylphenoxy)acetic acid, m. p. 95-96°.

From the residue remaining after the fractionation we isolated anthracene, m. p. 211-212°. Found: C 94.42; H 5.73%. $C_{14}H_{10}$. Calculated: C 94.38; H 5.61%.

A mixture test with pure anthracene showed no depression of melting point.

Fractionation residues from the experiments with m-cresol were combined and vacuum-distilled from a Claisen flask. In the fraction of b. p. 85-120° (10 mm) we identified 3,5-xylenol in the form of (3,5-xylyloxy)-acetic acid, m. p. 85-86°, and also p-cresol in the form of (p-tolyloxy)acetic acid, m. p. 135.5-136°. These two acids were separated by taking advantage of their different solubilities in hexane. The fraction of b. p. 153-155° (10 mm) appeared to contain phenyl o-tolyl ether. For this the literature gives b. p. 274° (735 mm). Found: C 84.26; H 6.90%. $C_{13}H_{12}O$. Calculated: C 84.7; H 6.52%.

Fractionation residues from the experiments with p-cresol were combined and vacuum-distilled from a Claisen flask. In the fraction of b. p. 110-130° (20 mm) we identified 2,5-xylenol in the form of (2,5-xylyloxy)-acetic acid, m. p. 117-118°. A mixture test with the (2,5-xylyloxy)acetic acid obtained in the experiments with o-cresol showed no depression of melting point. The fraction of b. p. 177-179° (16 mm) appeared to contain bis-p-tolyl ether. Found: C 85,17; H 6.77%. $C_{14}H_{14}O_{\circ}$ Calculated: C 84,85; H 7.06%.

<u>Composition of gaseous reaction products</u>. Data on the compositions of the gaseous products of the homogeneous destructive hydrogenation of o-, m-, and p-cresols at 490° at an initial hydrogen pressure of 300 atm and a reaction time of three hours are given in Table 4.

It may be concluded from Table 4 that the breakdown of the aromatic ring with formation of carbon monoxide and lower hydrocarbons proceeds most vigorously in the case of p-cresol. The possibility cannot be excluded that the carbon monoxide formed undergoes further transformations, not only into CO_2 as a result of reaction with steam, but also to some extent into hydrocarbons. It was therefore of interest to estimate the extent of the breakdown of the aromatic ring also from the composition of the hydrocarbon part of the gaseous products, account being taken of the methane formed by the demethylation of cresol and toluene. Some inaccuracy in this calculation is associated with the fact that benzene is formed not only from toluene, but also from phenol.

TABLE 3

Initial hydro-	Yield of	f liquid pro	ducts oth	er than wa	ater % by w	t on cresol	taken)
gen pressure (atm)	in all	Frac. I 6095°	Frac. II 95-113°	Frac. III 113175°	Frac, IV* 175-192°	Frac, V* 192-202,8°	Residue
			o ≁C	resol			
100 100 200 200 300 300	$\left \begin{array}{c} 87,4\\87,2\\81,7\\81,3\\74,9\\78,0\end{array}\right $	$ \begin{array}{c c} 2,9\\ 2,0\\ 6,2\\ 7,3\\ 14,2\\ 13,5 \end{array} $	8,1 7,7 11,5 12,5 13,4 13,7	3,8 4,7 3,4 4,5 3,3 4,1	$ \begin{array}{c} 22,6\\ 23,8\\ 28,7\\ 29,6\\ 29,8\\ 30,0 \end{array} $	40,0 38,9 21,4 18,8 8,4 9,4	10,0 10,1 10,5 8,1 5,8 7,3
			m-0	Cresol			
100 100 200 200 300 300	88,3 88,9 86,5 84,3 76,7 76,7	$ \begin{array}{c c} 0,7\\ 0,7\\ 2,9\\ 2,6\\ 7,1\\ 7,0\\ \end{array} $	$ \begin{array}{c c} 6,2\\ 5,9\\ 7,1\\ 7,8\\ 10,5\\ 11,0\\ \end{array} $	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	9,6 9,6 13,3 12,0 17,4 17,6	59,0 61,0 50,6 51,1 27,8 27,5	10,7 10,0 10,3 8,9 11,7 11,4
			p-Cre	sol			
100 100 200 200 300 300	85,5 84,4 76,5 76,4 71,6 69,8	1,5 1,4 5,8 6,1 8,2 8,9	5,8 5,9 9,0 9,8 9,5 9,6	$ \begin{array}{c} 6,0\\ 6,2\\ 4,9\\ 4,7\\ 4,4\\ 4,2 \end{array} $	19,8 20,0 21,5 21,0 21,3 21,0	41,9 40,9 25,0 26,2 19,0 18,5	10,5 10,0 10,0 8,9 9,2 7,6

Homogeneous Destructive Hydrogenation of Cresols at Various Initial Hydrogen Pressures (490°, three hours)

* In experiments with o-cresol: Fraction IV had b. p. 175-186.5° and Fraction V had b. p. 186.5-192°.

If it is assumed that one-half of the benzene formed arises from toluene, then the error in the calculation of the amount of methane does not exceed 1% by weight on the original cresol.*

The results of the calculation (% by weight on original cresol) are given below:

	o-Cresol	m-Cresol	p-Cresol
Total gaseous products	11.5	10.6	13.2
Amounts of these formed in the de-			
methylation of			
cresol	5,1	2.6	3.7
toluene	1.4	0.7	0.9
Gaseous decomposition products	5.0	7.3	8,6

TABLE 4

Compositions of Gaseous Reaction Products (% by volume)

Original cresol	H ₂	CH₄	C ₂ H ₈	C3H8	C4[110	со	CO2	CO + CO ₂ (moles % on original cresol)
o-Cresol m-Cresol p-Cresol	71,6 74,1 68,8	22,4 19,4 23,5	1,35 1,35 2,0	0,7 0,75 0,8	$0,25 \\ 0,35 \\ 0,5$	1,3 1,5 2,0	$0,4 \\ 0,2 \\ 0,4$	4,2 4,2 6,0

*Methyl radicals are partially consumed in the alkylation of cresol; this fact, however, cannot have a substantial effect on the results of the calculation. From the above approximate calculation it follows that the breakdown of the benzene nucleus of p-cresol under the conditions studied proceeds considerably more vigorously than that of o-cresol.

DISCUSSION OF EXPERIMENTAL RESULTS

In accordance with the views developed in communications from our laboratory [6, 7], the homogeneous destructive hydrogenation of aromatic hydrocarbons and their derivatives proceeds by a radical-chain mechanism with participation of molecular and atomic hydrogen. In the light of these views the results obtained in the present investigation on the homogeneous destructive hydrogenation of cresols are in accord with the following scheme (see also [8]):

$$OHC_6H_4CH_3 \longrightarrow OHC_6H_4CH_2 + H^{\circ}$$
(1a)

$$OHC_6H_4CH_3 \longrightarrow OC_6H_4CH_3 + H^{-1}$$
 (1b)

$$H+OHC_6H_4CH_3 \longrightarrow C_6H_4CH_3 + H_2O \text{ or } C_6H_5CH_3 + OH$$
(2a)

$$H + OHC_4H_4CH_3 \longrightarrow C_6H_4OH + CH_4 \quad \text{or} \quad C_6H_5OH + CH_3$$
(2b)

$$H + OHC_{0}H_{1}CH_{3} \longrightarrow CO + hydrocarbon radicals$$

$$\dot{R} + H_2 \longrightarrow RH + H' \tag{3}$$

$$\dot{C}H_3 + OHC_6H_4\dot{C}H_2 \longrightarrow OHC_6H_4C_2H_5$$
(4)

$$\dot{C}H_3 + \dot{C}_6H_4OH \longrightarrow OHC_6H_4CH_3$$
 (3)

$$OC_6H_4CH_3 + C_6H_4CH_3 \longrightarrow (CH_3C_6H_4)_2O$$
(0)

Reactions (1) are chain-initiation processes. However, the possibility cannot be excluded that reaction chains may be initiated also by the cleavage of $OHC_6H_4-CH_3$ bonds [9] (or $CH_3C_6H_4-OH$) and by the dissociation of molecular hydrogen [10]. Atomic hydrogen then reacts with cresol molecules by Reactions (2a), (2b), and (2c). The radicals R formed in Reactions (1) and (2) react with molecular hydrogen [Reaction (3)] with generation of atomic hydrogen. Reactions (4), (5), and (6) are chain-terminating processes which lead to the formation of ethylphenol, isomeric cresols, bistolyl ether, and other compounds.

At the same time there occurs further homogeneous destructive hydrogenation of toluene and phenol with formation of xylenols. The gaseous products undergo further transformations: carbon monoxide reacts with steam with formation of carbon dioxide; it is possible also that carbon monoxide reacts with hydrogen with formation of hydrocarbons (the over-all yield of gaseous products from the cleavage of the aromatic ring is greater than that calculated from their content of carbon monoxide and dioxide).

Our results (Table 3) indicate that homogeneous destructive hydrogenation proceeds most vigorously with o-cresol and least vigorously with m-cresol. Jones and Neuworth [8] found that the activation energy for the thermal decomposition of m-cresol is 6 kcal/mole greater than for o-cresol (the values are 75 and 69 kcal/mole, respectively). Hence, the results of our investigation confirm the view that there is a relation between homogeneous destructive hydrogenation and the thermal cleavage of the weakest bond in aromatic hydrocarbons and their derivatives.

Under the conditions studied demethylation and dehydroxylation of cresols are accompanied by cleavage of the aromatic rings of cresol and phenol, which is accelerated by increase in the pressure of hydrogen. The results of our investigation show that this reaction is least vigorous with o-cresol and proceeds 1.5-2 times as rapidly with p-cresol. m-Cresol, as far as can be judged from the results, reacts somewhat more slowly than p-cresol in this respect. Hence, the order found here differs from that found for the over-all rate of demethylation and dehydroxylation of the isomeric cresols.

We consider that the following is the probable explanation of the results. It is readily seen that the bond between a carbon atom carrying a hydroxy group and another carbon atom is weakened by the linkage of hydrogen to one of these two atoms:

121

151

101



However, addition of atomic hydrogen with formation of the radical (I) in accordance with the scheme assumed previously [7] leads mainly to the dehydroxylation of cresol with formation of a tolyl radical and water (or toluene and the OH radical). Hence, it may be supposed that the cleavage of an aromatic ring with formation of carbon monoxide and C_1-C_4 (and also possibly C_5) hydrocarbons proceeds mainly as a result of the union of a hydrogen atom in the ortho position to the hydroxy group. The probability of such cleavage in o-cresol is approximately one-half of that of its occurrence in m- and p-cresols, because the tendency for the radical



to undergo demethylation is very great.

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SUMMARY

1. An investigation was made of the homogeneous destructive hydrogenation of toluene, phenol, and o-m-, and p-cresols at 490° at initial hydrogen pressures of 100-300 atm.

2. Under these conditions the demethylation of toluene is almost twice as fast as the dehydroxylation of phenol.

3. By the homogeneous destructive hydrogenation of cresols yields of phenol of up to 30% by weight on the cresol can be attained.

4. With respect to the over-all rate of demethylation and dehydroxylation the cresols are in the order: o-cresol > p-cresol > m-cresol.

5. As well as demethylation and dehydroxylation, cresols, like phenol, undergo simultaneous cleavage of the aromatic ring. The tendency for cleavage to occur falls in the order. p-cresol > m-cresol > o-cresol.

6. The question of the mechanism of the cleavage of the aromatic ring in cresols was examined and a general radical-chain scheme for the homogeneous destructive hydrogenation of cresols was proposed; the scheme is confirmed by the results obtained on the compositions of the products of reaction-chain termination.

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