Isoöctane produced at 350° a liquid with n^{25}D 1.3880, traces of reaction with nitrating mixture.

Diisoamyl produced at 300, 325 and 350° a liquid with n^{25}D 1.4080, 1.4090 and 1.4090, respectively. The combined product contained 9.7% of olefins and traces of aromatics.

Summary

In the presence of nickel–alumina catalyst, the normal paraffins n-octane and n-decane undergo dehydrogenation accompanied by cyclization to aromatic hydrocarbons. A splitting forming toluene and methane also takes place which is not observed with catalysts of platinum charcoal or chromium oxide. Isomerization of the normal paraffins also was noted.

Aromatization of Fatty Alcohols

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The role of various substituents of mixed catalysts in heterogeneous catalysis such as promoter and carrier (support) action has assumed prime importance in our present knowledge of the subject. While in many cases it may be difficult to distinguish between catalyst, promoter, and carrier phenomena, the fact remains that only one reaction is catalyzed in one specific direction. There are, however, mixed catalysts which accomplish two or more different reactions, due to the action of each component of the mixed catalyst working in its own specific direction. It is proposed to call such catalysts "complex-action" catalysts.

In such cases the resulting reaction is a series of parallel or consecutive steps leading to the formation of desired product.

Thus, by combining nickel oxide and alumina, it was possible to obtain directly from camphor, isocamphane by simultaneous reduction, dehydration and hydrogenation.[1,2] By combining a polymerizing and hydrogenating catalyst, isooctane was obtained in one step from isobutylene and hydrogen (hydropolymerization).[3,4] The dehydropolymerization of ethylene[5] represents another example of these types of reactions.

In the development of these ideas a simultaneous combined reaction of dehydration and dehydrogenation of aliphatic alcohols was carried out. The dehydration of fatty alcohols results in the formation of olefin hydrocarbons which by further dehydrogenation can produce more un-saturated material such as diolefins and acetylenes. It was of particular interest to perform this type of simultaneous reaction with the fatty alcohols containing a chain of six or more carbon atoms in order to see whether a more complete dehydrogenation of this chain could take place causing cyclization and formation of aromatic hydrocarbons. For these reactions a mixed dehydrating–dehydrocyclizing catalyst was required.

In this work an alumina-chromium oxide catalyst was used; alumina was the dehydrating and chromium oxide the dehydrogenating and cyclizing catalyst. The simultaneous dehydration and dehydrocyclization of n-hexyl, n-heptyl and n-octyl alcohols, and di-n-propylcarbinol was performed. As expected it was found that the simultaneous reaction took place with the production of aromatic hydrocarbons according to the scheme

$$C_nH_{(2n+1)}OH \longrightarrow C_nH_{2n} + H_2O \longrightarrow C_nH_{2n-6} + 3H_2$$
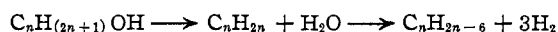
In addition to this reaction, dehydrogenation of the alcohols to aldehydes also took place as shown by the presence of carbon dioxide and carbon monoxide in the reaction gases.

For the fatty alcohols containing six and seven carbon atoms, cyclization of the olefin produced gave the corresponding aromatic hydrocarbon. When n-octyl alcohol was subjected to this reaction, a more complex reaction product was obtained. As expected, the eight-carbon chain cyclized to o-xylene and ethylbenzene. In addition, however, m- and p-xylene and toluene were identified. Thus, with this alcohol it is evident that isomerization occurs and m- and p-xylene are produced by the migration of a methyl

(1) Ipatieff, *Ber.*, **45**, 3205 (1912).
(2) Ipatieff and Matov, *J. Russ. Phys.-Chem. Soc.*, **44**, 1695 (1912).
(3) Ipatieff and Komarewsky, THIS JOURNAL, **59**, 720 (1937).
(4) Ipatieff and Komarewsky, *Ind. Eng. Chem.*, **29**, 958 (1937).
(5) Komarewsky and Balai, *ibid.*, **30**, 1051 (1938).

TABLE I

Expt.	Alcohol charged	G.	Temp., °C.	Recov., g.	$n^{25}D$	$n^{25}D$ without bottoms	Aromatics % by weight By $n^{25}D$	By H	Aromatics found	M.p. °C.	Aromatics identified as	Total evolved, cc.	H_2	CO	CO_2	Total olefins	Paraffins	Paraffin index
1	n-Heptyl	16.3	450	11.4	1.4065	1.4035	7.8	..	Toluene	70	2,4-Dinitrotoluene	....	..	..	..	..	..	..
2	n-Heptyl	30.2	500	14.6	1.4660	1.4554	58.1	66.0	Toluene	70	2,4-Dinitrotoluene	14,420	67.0	3.8	7.1	5.0	17.1	1.8
3	Di-n-propyl carbinol	30.9	468	21.85	1.4143	1.4068	7.2	6.7	Toluene	70	2,4-Dinitrotoluene	4,580	48.8	2.6	11.1	22.0	15.5	1.7
4	Di-n-propyl carbinol	26.0	480	16.3	1.4192	1.4136	12.5	13.0	Toluene	70	2,4-Dinitrotoluene	5,520	51.1	2.9	10.0	20.6	15.4	1.8
5	n-Hexyl	26.1	467	18.3	1.4065	1.4022	7.5	7.6	Benzene	89	m-Dinitrobenzene	3,480	62.1	2.1	9.2	15.3	11.3	1.8
6	n-Hexyl	17.8	500	10.4	1.4405	1.4377	38.0	37.7	Benzene	89	m-Dinitrobenzene	7,140	58.2	2.2	5.4	18.3	15.9	1.7
7	n-Octyl	39.0	475	17.5	1.4533	....	..	47.2	Toluene—3%	70	2,4-Dinitrotoluene	12,000	63.5	6.4	6.8	11.8	11.5	3.2
									Ethylbenzene—4.5%	121	Benzoic acid							
									*o-Xylene	127	o-Phthalic acid anhydride							
									m-Xylene—7%	64	Dimethyl ester of meta-phthalic acid							
									p-Xylene	137–138	Dimethyl ester of tere-phthalic acid							
									Higher boiling aromatics—32.7%									

* Traces of m-xylene.

group. Toluene probably is formed by splitting off of a methyl group. Besides, higher boiling unidentified aromatics were found in the reaction product.

The dehydration of alcohols over alumina catalyst takes place with measurable velocities even at 200–300°; however, the dehydrogenation of the olefin produced requires higher temperatures. Therefore the experiments were conducted at 450° and higher. At these temperatures the dehydration takes place with non-measurable speed so that the total reaction might be considered kinetically as being a simple monomolecular (found experimentally) dehydrogenation of olefin hydrocarbons. Due to excellent constancy and reproducibility of the reaction speed an attempt was made to evaluate the energy of activation.

Experimental Part

Apparatus and Procedure.—The alcohols were passed at a rate of 7–10 cc. per hour through a 14-mm. inside diameter glass tube filled with 50 g. of 8–10 mesh catalyst, in a slow stream of nitrogen. The tube was contained in a horizontal electric furnace. The liquid products were condensed by means of a water condenser and an ice trap.

Alcohols.—n-Hexyl alcohol, b. p. 153–156°, $n^{25}D$ 1.4170; n-heptyl alcohol, b. p. 172–176°, $n^{25}D$ 1.4222; n-octyl alcohol, b. p. 196.0–197.0°, $n^{25}D$ 1.4295; di-n-propylcarbinol, b. p. 151–154°, $n^{25}D$ 1.4159.

Catalyst.—The catalyst was prepared by the simultaneous precipitation of chromium and aluminum hydroxides from an alkaline solution of aluminate and chromite by nitric acid. The precipitate was washed anion free, dried and reduced at 450° in a stream of hydrogen. The chromium oxide content was 25%.

Analysis of the Products.—The first exploratory experiment indicated that:

1. A complete decomposition of the alcohols took place, since no traces of alcohols could be detected in the product.

2. The formation of carbon monoxide and dioxide in the gases showed that a certain amount of the alcohol charged underwent a dehydrogenation to aldehyde with a consecutive decomposition of the latter. The decomposition of the aldehyde formed is complete since no undecomposed aldehyde was detected in the liquid reaction product by the sodium bisulfite method. Thus the amount of the aldehyde formed can be calculated from the amount of oxygen evolved in the gas in the form of carbon monoxide and dioxide. Consequently, the amount of hydrogen formed in the reaction gas belongs to two reactions: (a) alcohol dehydrogenation to aldehyde; and (b) olefin cyclization to aromatics.

3. The boiling points of the liquid reaction products are always lower than those of the charged alcohol and usually correspond to the boiling points of the mixture of corresponding olefin and aromatic hydrocarbons. Small

TABLE II

Expt.	Alcohol charged	Temp., °C.	% by weight of alcohol charged			Cyclization of dehydrated alc., % by weight
			Dehydrated	Dehydrogenated	Cyclized	
2	n-Heptyl	500	55.5	44.5	32.0	57.7
3	Di-n-propylcarbinol	468	80.5	19.5	4.7	5.9
4	Di-n-propylcarbinol	480	74.8	25.2	8.2	11.0
5	n-Hexyl	467	83.3	16.7	5.3	6.3
6	n-Hexyl	500	76.1	23.9	12.0	15.8
7	n-Octyl	475	64.3	35.7	21.2	33.0

(about 5%) higher boiling bottoms probably are formed due to polymerization of unsaturated and hydrocarbon fragments from aldehyde decomposition. These bottoms have a very high refractive index (incomparably higher than the corresponding aldehyde or alcohols) which indicates that unreacted alcohol, or undecomposed aldehyde, is absent in the liquid reaction product.

Taking these facts into consideration, the following analytical procedure was applied.

Gas Analysis.—The gas was analyzed by the Göckel method. The amount of alcohol dehydrogenated to aldehyde (or ketone) and the amount of aromatic hydrocarbon formed was calculated, as follows.

Total gas evolved, 5520 cc.; carbon dioxide content, 10.0%; carbon monoxide content, 2.90%. Oxygen, as calculated from carbon dioxide and carbon monoxide, 0.903 g. This oxygen corresponds to 6.55 g. of alcohol dehydrogenated to ketone, producing 1265 cc. of hydrogen. Total hydrogen evolved, 2820 cc. (N. T. P.). Hydrogen evolved from toluene formation 2820 − 1265 = 1555 cc. This corresponds to 2.12 g. of toluene or 13.0% in the product, or 8.2% on alcohol charged.[6]

Liquid Analysis.—The liquid products of the reaction were separated from water (formed on dehydration), dried with calcium chloride (since no undecomposed alcohol was found in the product) and fractionated by means of a 36-inch (91-cm.) distilling column of the Podbielniak type. As mentioned previously, the boiling point of the product was typical of a mixture of corresponding unsaturated and aromatic hydrocarbons. The combined fractions were analyzed for olefins by sulfuric acid. The amount of aromatics formed was checked also by the refractive indices of the product (without the bottoms) using refractive index curves. In the case of octyl alcohol the product was hydrogenated selectively before fractionation in order to eliminate the olefins. The results of the experiments are given in Tables I and II.

Kinetics of the Reaction

Experiments 3, 4, 5, and 6 were carried out under carefully controlled conditions, each time with a freshly regenerated catalyst. The reaction took place with a constant speed during a sufficiently long time (two to four hours). Thus it was possible to evaluate the kinetic constants and calculate the energy of activation.

(6) Data from Experiment 4.

Calculations from the experimental data showed that the reaction of aromatization is of the first order and the formula $K = \frac{2.303}{t} \log \frac{a}{a - x}$ (t, time, a, the amount taken into the reaction; and x, the amount of product in per cent.) can be applied. The energies of activation, Q, were calculated using the formula

$$2.303 \log \frac{K_2}{K_1} = \frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where K_1 and K_2 were the velocity constants, and T_1 and T_2 the corresponding absolute temperature. The constants were determined for two reactions: (1) alcohol aromatization, and (2) alcohol dehydrogenation to aldehyde (or ketone).

Table III presents the results of these calculations.

TABLE III

Alcohol	Cal./mole, Q for aromatization	Q for aldehyde (or ketone) formation
n-Heptyl alcohol	59,700	
Di-n-propylcarbinol	57,600	31,100
n-Hexyl alcohol	62,000	14,200

Summary

1.   Under the action of a mixed, chromic oxide–alumina catalyst, the fatty alcohols undergo a complex reaction involving dehydration, dehydrogenation, and cyclization producing aromatic hydrocarbons.

2.   The reaction was accomplished with alcohols containing six, seven, and eight carbon atoms.

3.   Each component of the chromic oxide–alumina catalyst influenced the reaction in its own specific direction, alumina acting as dehydration and chromium oxide as a dehydrogenation and cyclization catalyst.

4.   It is proposed to name this type of mixed catalysts "complex-action catalysts."