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Catalytic Dehydration and Dehydrogenation of Butyl and Amyl Alcohols

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In a previous article[1] a simultaneous dehydration–dehydrogenation of aliphatic alcohols containing six, seven and eight carbon atoms was described. As a result of this reaction a direct formation of aromatic hydrocarbons from aliphatic alcohols took place. This phenomenon was achieved by the use of a complex action catalyst[1] consisting of alumina (dehydrating agent) and chromia (dehydrogenating agent).

The present article describes the action of similar chromia–alumina catalysts on the alcohols containing four and five carbon atoms. As was expected, the same combined catalytic effect took place with these alcohols, resulting in the formation of diolefinic hydrocarbons. The reaction was dehydration of alcohol with consecutive dehydrogenation of olefin formed. Alumina alone (Expts. 4 and 7, Table II) under the conditions studied produced a pure dehydration of alcohol to olefin.

In addition to the above combined reaction of dehydration–dehydrogenation, some direct dehydrogenation of alcohols to aldehyde with subsequent decomposition of the aldehyde formed took place. This fact is indicated by the formation of oxides of carbon and paraffins in the reaction gases.[2]

Experimental Part

Apparatus and Procedure.—The reactions were carried out by passing the alcohols at a rate of 15–40 cc. per hour into the top of a 15 mm. inside diameter quartz tube filled with 100 cc. of 8–10 mesh catalyst. The liquid was fed by means of a Tropsch–Mattox adjustable feed pump.[3] The space (10 cm.) above the catalyst was filled with quartz chips for preheating the alcohols charged. The catalyst tube was contained in a vertical electric furnace with an automatic temperature control.

In order to favor the equilibrium of the reaction, the experiments were carried out at reduced pressure. The vacuum (130–300 mm.) was maintained by means of a "Cenco" gas collecting vacuum pump and an automatic pressure regulator. The last consisted of a U-tube arrangement as shown in Fig. 1. Any desired pressure could be obtained in the apparatus by setting the pressure first in the reference flask and then in the apparatus by means of stopcocks A and B. The automatic regulation of the pressure was controlled by the mercury in the U-tube making contact with the nichrome wire lead at C, starting and stopping the pump. The vacuum pump motor was operated through a mercury switch relay to reduce arcing at the contact point of the nichrome wire lead in the U-tube.

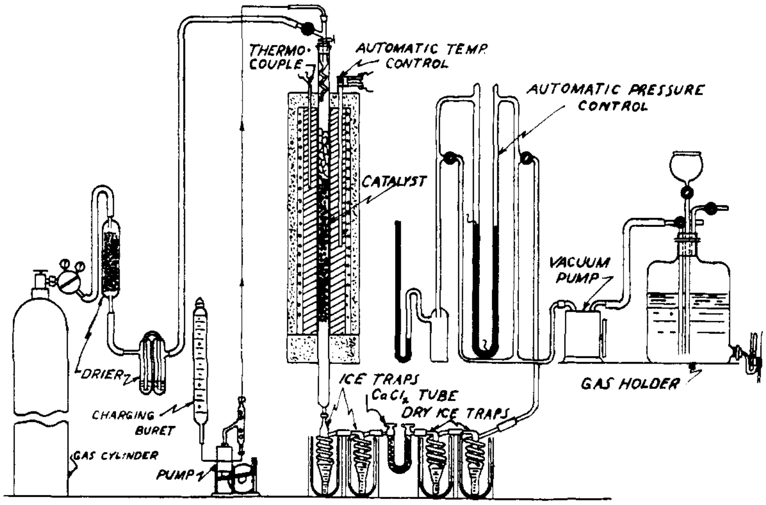

Fig. 1.

The reaction products from C_5 alcohols were collected in two graduated receivers cooled with ice, and two with an acetone–dry-ice mixture. A calcium chloride tube was placed between the second and third receiver to remove last traces of water formed in the reaction. The non-condensable gas was collected in a gas holder. The diagram of the apparatus is represented in Fig. 1. The acetone–dry-ice receivers were omitted when C_4 alcohols were charged. After removing the water as before, the gases passed to the gas holder.

TABLE I

IDENTIFICATION OF DIOLEFINS

Diolefin	Derivative prepared	M. p. of derivative
1,3-Butadiene	*cis* - Δ^4 - Tetrahydrophthalic anhydride	104
Piperylene	*cis* - 6 - Methyl - Δ^4 - tetrahydrophthalic anhydride	62
Isoprene	*cis* - 5 - Methyl - Δ^4 - tetrahydrophthalic anhydride	63–64

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[1] Komarewsky, Riesz and Thodos, THIS JOURNAL, **61**, 2525 (1939).

[2] C. D. Hurd, "The Pyrolysis of Carbon Compounds," Chemical Catalog Company, New York, N. Y., 1929, p. 238.

[3] Tropsch and Mattox, *Ind. Eng. Chem.*, **26**, 1338 (1934).

TABLE II

RESULTS OF THE SIMULTANEOUS DEHYDRATION AND DEHYDROGENATION OF BUTYL AND AMYL ALCOHOLS

Expt.	Alcohol charged	Temp., °C.	Press., mm.	Space vel.	Diolefin formed		Olefin formed, wt. %	Carbon formed, wt. %	Gas analysis, %				
					Name	Yield, wt. %			CO	CO_2	H_2	Total olefin	Paraffin
1	*n*-Butyl	575	150	0.15	Butadiene-1,3	1.8	22.4	22.1	..	..	..	..	..
2	*n*-Butyl	600	133	.17	Butadiene-1,3	5.1	20.4	14.4	7.5	4.7	66.0	12.0	9.7
3	*n*-Butyl	625	128	.23	Butadiene-1,3	7.4	21.1	16.3	4.6	5.5	60.1	16.9	12.9
4[a]	*n*-Butyl	600	133	.17	Butadiene-1,3	0.0	68.0	3.0	..	..	..	..	..
5	*n*-Amyl	575	155	.33	Piperylene	5.5	46.9	..	..	..	..	..	..
6	*n*-Amyl	600	130	.38	Piperylene	12.5	40.6	12.4	6.1	6.0	65.5	12.0	10.4
7[a]	*n*-Amyl	600	130	.35	Piperylene	0.0	73.1	1.5	..	..	..	..	..
8	Isoamyl	600	130	.34	Isoprene	15.9	49.3	2.2	5.9	8.0	49.0	9.1	25.3

[a] Pure alumina catalyst.

Analysis of the Product.—The combined liquid products from C_5 alcohols was separated from water (formed on dehydration), dried with calcium chloride (since no undecomposed alcohol was found in the product), and distilled in a 36-inch (91-cm.) distilling column of the Podbielniak type. The distillation indicated that olefins and diolefins were present with only traces of polymers.

The diolefins formed were analyzed by means of the maleic anhydride method of Tropsch and Mattox[4] and identified by the preparation of maleic anhydride addition compounds (see Table I) following the procedure of Birch and Scott.[5]

Non-condensable gases were analyzed by the Goeckel method.[6]

Table II represents the results of the experiments.

Alcohols.—*n*-Amyl alcohol, b. p. 135.2–135.7 (748 mm.), $n^{20}\mathrm{D}$ −1.4105; *n*-butyl alcohol, b. p. 117.5–118.0, $n^{20}\mathrm{D}$ −1.3993; isobutyl carbinol, b. p. 132–132.5, $n^{20}\mathrm{D}$ −1.4102.

Catalyst.—A 4% chromia–96% alumina catalyst was used in the experiments. It was prepared by impregnating activated alumina with a calculated amount of chromium nitrate $Cr(NO_3)_3 \cdot 9H_2O$ dissolved in water. When all the chromium nitrate solution had been adsorbed on the alumina, the catalyst was dried and reduced in a stream of hydrogen at 600°. Grade A activated alumina of the Aluminum Corporation of America sold as a drying agent, was used as a dehydrating catalyst.

A certain amount of carbon was deposited on the catalyst during each experiment. It was necessary to remove this carbon before proceeding to the next experiment. The catalyst tube was allowed to cool to between 300–350°, and was flushed with nitrogen to remove all hydrogen left in the tube from the reaction. Oxygen was then introduced to the catalyst tube and the carbon oxidized. After burning off the carbon, the tube was again flushed with nitrogen, the temperature raised to the desired point for the next experiment, and hydrogen passed over the catalyst for two hours.

Summary

1. Under the action of a mixed chromic oxide–alumina catalyst, the fatty alcohols containing four and five carbon atoms undergo a complex reaction involving dehydration and dehydrogenation, producing diolefinic hydrocarbons.

2. 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 catalyst.

3. Alumina alone produced a pure dehydration of alcohol to olefin.

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[4] Tropsch and Mattox, *Ind. Eng. Chem., Anal., Ed.*, **6**, 104 (1934).

[5] Birch and Scott, *Ind. Eng. Chem.*, **24**, 49 (1932).

[6] The Universal Oil Products Laboratory Test Methods of Petroleum and its Products, Universal Oil Products Company, Chicago, Illinois, 1937, p. 162.