

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Hydrogenolysis of Aliphatic Alcohols¹

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In the course of an extended study on the action of metallic oxide catalysts on alcohols it was found³ that chromium oxide exhibited not only the conventional reactions of dehydration and dehydrogenation, but also the secondary reaction of condensation. The product of the simultaneous dehydrogenation-condensation of primary aliphatic alcohols of " n " carbon atoms proved to be a symmetrical ketone of " $2n - 1$ " carbon atoms.

The experimental results reported herein were obtained from a continuation of this study with other oxide catalysts.

Experimental

Apparatus and Procedure.—The apparatus and procedure employed for the atmospheric and the superatmospheric autoclave experiments were similar to previous investigations.³

The high pressure flow system was designed to permit continuous operation at pressures up to 200 atmospheres. The reactant was fed to the reaction tube by a Hills-McCanna proportionating pump capable of delivering uniform flow rates as low as 15 cc. per hour against the operating pressure. The stainless steel reaction tube, catalyst capacity 50 cc., was equipped with a preheating section and encased in a vertical electric furnace with automatic temperature control. The operating pressure was controlled by a Taylor back pressure regulator. As a safety precaution, a rupture disk, release pressure 220 atmospheres, with connections to a suitable vent line was installed. The reaction product, after release to atmospheric pressure through the back pressure regulator, entered the usual series of water and Dry Ice condensers. The non-condensable gas was collected in a gas holder.

Catalysts.—The catalysts used for this investigation were prepared by co-precipitation methods. In cases of multi-component catalysts where any doubt as to composition might exist, the composition was checked by analysis.

Analysis of Products.—The liquid product was distilled in either a low or high temperature super-cal Heli Grid Podbielniak column, or in both, depending on the boiling range of the product. The hydrocarbon fraction was then treated with sulfuric acid of varied concentrations or bromine to effect the separation of the olefinic from the paraffinic hydrocarbons.

Discussion of Results

Vanadium pentoxide, known to be a mixed dehydration-dehydrogenation catalyst, was found to catalyze also the secondary reaction of hydrogenation. Primary aliphatic alcohols, when subjected to the action of vanadium pentoxide catalyst at 380° and atmospheric pressure, were converted to paraffinic hydrocarbons of the same number of carbon atoms with an average yield of 43.0%.

The conversion of primary alcohols to paraffinic hydrocarbons has been reported by several in-

vestigators.⁴ In each case the synthesis involved a rupture of the carbon to carbon bond, thus reducing the carbon chain length by one carbon atom. The catalytic conversion presented in this article differs in that no diminution of the chain length occurs.

The combination of a dehydration catalyst, aluminum oxide with vanadium pentoxide (35% V_2O_5 , 65% Al_2O_3) gave a noticeable increase (50% conversion) in the yield of paraffinic hydrocarbon. On the other hand, the combination of an alcohol dehydrogenation catalyst, copper, with vanadium pentoxide (35% Cu, 65% V_2O_5) gave a poorer yield (37.5%) than the pure vanadium pentoxide.

The general utility of the paraffinic hydrocarbon synthesis was demonstrated by the successful conversion of *n*-butyl, *i*-butyl, *n*-hexyl and *n*-octyl alcohols to the corresponding paraffinic hydrocarbons.

A material increase in the conversion (68.5% yield) was obtained by the use of 40 atmospheres pressure of hydrogen in a continuous high pressure flow system. A similar experiment carried out in a rotating autoclave gave unsatisfactory results (0.0% yield).

The combination of the most widely used hydrogenation catalyst, nickel, in small amounts with vanadium pentoxide-aluminum oxide catalysts gave a marked increase in the scission of the carbon to carbon bonds with the production of methane and ethane. Nickel-alumina catalysts of varied composition were unsatisfactory for the same reason.

Two other oxide catalysts molybdenum trioxide and tungsten trioxide were investigated. The data obtained were in agreement with that of previous investigators listing molybdenum trioxide as a mixed dehydration-dehydrogenation catalyst, and tungsten trioxide as predominantly a dehydration catalyst. Neither catalyst exhibited secondary reactions such as found with chromium oxide and vanadium pentoxide.

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Summary

1. Primary aliphatic alcohols when subjected to the action of vanadium pentoxide catalyst at 380–400° and atmospheric pressure were converted to paraffinic hydrocarbons with the same number of carbon atoms.

(4) Badin, *ibid.*, **65**, 1809 (1943); Suen and Fan, *ibid.*, **64**, 1460 (1942); Böeseken and van Senden, *Rec. trav. chim.*, **32**, 23 (1913); Wojcik and Adkins, *THIS JOURNAL*, **55**, 1293 (1933); Gault, Palfray and Tsu, *Compt. rend.*, **209**, 999 (1939).

(1) Presented before the Division of Organic Chemistry at the Chicago Meeting of the American Chemical Society, September 9, 1946.

(2) Universal Oil Products Company Research Fellow.

(3) Komarewsky and Coley, *THIS JOURNAL*, **63**, 700, 3269 (1941); Komarewsky and Kritchevsky, *ibid.*, **65**, 547 (1943).

2. The use of a co-precipitated vanadium pentoxide-aluminum oxide catalyst and super-atmospheric pressure resulted in substantial improvement in the conversion of alcohols to paraffinic hydrocarbons.

3. The general utility of the paraffinic hydrocarbon synthesis was demonstrated by successful conversion of *n*-butyl, *i*-butyl, *n*-hexyl and *n*-octyl alcohols to the corresponding hydrocarbons.

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Condensation of Acetylene with Acetone and Other Ketones

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The condensation of acetone and acetylene into dimethylethynylcarbinol dates from Merling's patents² in 1914, and the extension of this work by Locquin and Sung Wouseng.³ They used sodium or sodamide as condensing agents. The method was adopted by "Organic Syntheses"⁴ with a stated yield of 40-46%.

It was mentioned by Merling² that liquid ammonia might serve as a medium for the preparation of ethynylcarbinols, but he cited no examples making use of this procedure. McGrew and Adams⁵ did use such a method in their synthesis (50% yield) of 1-pentyn-3-ol from propionaldehyde and sodium acetylide. Two patents⁶ issued in 1938, employing sodamide catalyst in liquid ammonia solution, mention yields of 81-99% in the acetylene-acetone reaction. The improvement in yield, according to Kreimeier's claims, were due to the presence of a trace of hydrated ferric nitrate as catalyst during the preparation of the sodamide. Macallum used this same catalyst but specified improvement in the method of neutralization of the alkali by ammonium chloride at the end of the run. Since this time several other investigators⁷ have used these procedures but yields have always been below 90%, actually 67-88%.

We are indebted to Dr. Glen H. Morey of Commercial Solvents Corporation for suggesting that traces of water in this reaction might exert an adverse effect on the yield. Experiments conducted under strictly anhydrous conditions showed that this was indeed true. Yields ranged from 86-93% when acetone was used containing no more than 0.04% water; but when 0.17% of

total water was present in either the acetone or the ammonia, yields dropped to 68-75%, and when 0.54% water was present, yields were only 49-52%.

The same held for methyl ethyl ketone. The tertiary alcohol was obtained in 94% yield when an anhydrous ketone (0.003% water) was taken at the start, but only a 75% yield was obtained if 0.01% of water was present. Campbell, Campbell and Eby⁸ reported yields of 60-72% for this preparation when hydrated ferric nitrate was used in the preparation of sodamide catalyst.

As might be surmised, the water of hydration in ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was found to affect the yield of carbinol adversely, since it provided an unavoidable 0.138% of water. When used with otherwise anhydrous acetone (0.003% water), the yield of dimethylethynylcarbinol was 81%.

Experimental

Samples of anhydrous acetone (0.042 and 0.003% water) and methyl ethyl ketone (0.003% water) were kindly furnished by Commercial Solvents Corporation. Drying was effected with "Drierite" (75 g. per 500 g. of the ketone), shaking the bottles occasionally during three days.

In the experiments described below wherein anhydrous conditions were maintained, ammonia was dried with sodium and distilled directly into the reaction flask. All the glassware used was dried in an oven for three hours before use. Just before the materials were added into the reaction flask, air, dried by passage through two towers containing anhydrous $\text{Mg}(\text{ClO}_4)_2$, was passed through the apparatus for one hour. Openings into the system were protected by tubes of anhydrous. Acetylene was dried by passage through a trap at -78° (which also condensed the acetone from the acetylene), then through the same drying towers of anhydrous which were used to dry the air. The sodium for use in the reaction was cleaned under kerosene of all oxide coating and used promptly.

Preparation of Dimethylethynylcarbinol with Anhydrous Conditions.—To 300 ml. of liquid ammonia which had been distilled into a liter 3-necked flask, cooled by Dry Ice and acetone to -50° , was added 4.6 g. (0.2 mole) of sodium in small pieces. The flask was equipped with a mercury-sealed stirrer, an inlet tube extending to the bottom of the flask, and an outlet tube. Dry acetylene was passed into the solution at the rate of 15-20 liters an hour until the blue color of sodium was discharged, leaving a suspension of white sodium acetylide. This required thirty minutes. The inlet tube was replaced by a dropping funnel containing 14.6 ml. (11.6 g. or 0.2 mole) of dry

(1) Holder of Commercial Solvents Corporation Fellowship, 1938-1940.

(2) Merling and F. Bayer and Co., German Patents 280,226, 285,770, 286,920, 289,800, 291,185; *Chem. Zentr.*, **85**, II, 1370 (1914); **86**, II, 508, 932 (1915); **87**, I, 815, 317 (1916).

(3) Locquin and Sung Wouseng, *Compt. rend.*, **174**, 1427 (1922); *Bull. soc. chim.*, (4) **35**, 597, 604 (1924); Sung Wouseng, *Ann. chim.*, [10] **1**, 343 (1924).

(4) Coffman, "Organic Syntheses," **20**, 40 (1940).

(5) McGrew and Adams, *THIS JOURNAL*, **59**, 1497 (1937).

(6) Kreimeier, U. S. Patent 2,106,180 (1938); Macallum, *ibid.*, 2,125,384 (1938).

(7) Froning and Hennion, *THIS JOURNAL*, **62**, 653 (1940); Taylor and Shenk, *ibid.*, **63**, 2756 (1941); Hennion and Murray, *ibid.*, **64**, 1220 (1942); Backer and Blass, *Rec. trav. chim.*, **61**, 785, 924 (1942); Henne and Greenlee, *THIS JOURNAL*, **67**, 484 (1945); Newman, Fones and Booth, *ibid.*, **67**, 1053 (1945).

(8) Campbell, Campbell and Eby, *ibid.*, **60**, 2882 (1938).