[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE TUNG LI OIL WORKS, CHUNGKING, CHINA]

Catalytic Hydrogenation of Heptaldehyde in Vapor Phase

BY TZENG-JIUEQ SUEN AND SIMONE FAN

Heptaldehyde has been reduced in various ways by different investigators. Normal heptyl alcohol is obtained when heptaldehyde is treated with zinc in acetic acid solution,[1] with sodium amalgam and acetic acid,[2] with iron and acetic acid,[3] with sodium in toluene and acetic acid,[4] or by electrolytic reduction.[5] Catalytic reduction with colloidal platinum catalyst in dilute acetic acid solution[6] or with a specially prepared platinum oxide catalyst in alcohol solution with a small amount of ferrous chloride,[7] yields the same product. Clemmensen[8] claimed that n-heptane can be obtained by reducing heptaldehyde with amalgamated zinc and hydrochloric acid, although this method has been discredited by other investigators.[9] When heptaldehyde was hydrogenated under pressure, Riedel[10] claimed to have obtained n-heptyl alcohol and some diheptyl ether with mixed oxides of nickel, cobalt and copper as catalyst, and Braun and Manz[11] obtained n-heptyl alcohol and some hydroxyl compound with fourteen carbon atoms using nickel as catalyst.

In the present investigation, heptaldehyde was hydrogenated in vapor phase under atmospheric pressure with a nickel catalyst. A basically different reaction was observed. The main reaction product was found to be n-hexane, and some n-heptyl alcohol also was formed. The experimental procedure and the identification of the products are reported here, while the effect of operating conditions on the results will be presented in a subsequent paper.

Experimental

Apparatus and Procedure.—The apparatus was more or less conventional. The reactor consisted of a 25-mm.

o. d. Pyrex glass tubing, which was placed vertically in an electric furnace, heated over a 50-cm. length. A thermocouple well, also consisting of a Pyrex tubing, was inserted in the center of the catalyst bed, which amounted to 43.4 g. of nickel carbonate–kieselguhr mass (see below), occupying the middle 12 cm. of the reaction tube. The top of reaction tube was fitted with a heptaldehyde inlet and a hydrogen gas inlet, while at bottom the exit gas was passed successively through a condenser, a receiver, a trap immersed in ice–salt mixture, and a wet gas meter. The heptaldehyde was fed through a buret, the rate of flow being checked frequently with a stop watch. The rate of hydrogen used was measured by a bubble-meter.

The experiment was repeated several times under identical conditions, and practically identical results were obtained. The average conditions for the runs were as follows: temperature of reaction $250 \pm 2°$, hydrogen rate 8.6 liters (N.T.P.) per hour, heptaldehyde rate 22 g. per hour, the molecular ratio of hydrogen to heptaldehyde being about 2:1. The duration of each run was for two to four hours. The liquid products obtained consisted of an upper layer of organic compounds amounting to 80–90% by volume of heptaldehyde used, and a lower layer of water. It must be mentioned that as no dry-ice or liquid air was available, the reaction products could not be cooled below the temperature of ice–salt mixture. A certain amount of the hydrocarbon formed remained uncondensed in the gaseous products, which on the average amounted to 4.4 liters (N.T.P.) for every 10 g. of heptaldehyde used.

Preparation of Catalyst.—The nickel catalyst was prepared by a method similar to Fischer's.[12] A hundred and fifty grams of E. Merck c. p. grade nickel nitrate was dissolved in 600 ml. of water, mixed with 30 g. of kieselguhr, and treated with 150 g. of c. p. sodium carbonate dissolved in 300 ml. of water. The reaction mass was brought to boiling for a short time, filtered, washed with hot water, dried at 110°, pressed and broken into granules of 8–10 mesh size. A portion of 43.4 g. was packed in the reaction tube. Before use, it was reduced at 420° with hydrogen for 4.2 hours at a rate of about 10 liters per hour.

Materials.—The heptaldehyde was prepared from castor oil,[13] twice fractionated with a 40-cm. long column packed with broken glass. The portion distilled over at 152–154° was collected, n^{20}D 1.4132. The hydrogen was prepared with iron and hydrochloric acid, stored in glass reservoirs, purified by successively washing with potassium permanganate, sodium hydroxide, alkaline pyrogallol, and concentrated sulfuric acid before use.

Identification of the Products.—The liquid products in the receiver and the trap were combined. The lower layer was separated and the upper layer after being dried with anhydrous sodium sulfate, fractionated in a 7-mm. i. d. 80-cm. long spiral column. A typical distillation curve

(1) Bouis and Carlet, *Ann.*, **124**, 352 (1862); Krafft, *Ber.*, **16**, 1723 (1883).

(2) Schorlemmer, *Ann.*, **177**, 303 (1875); Cross, *ibid.*, **189**, 2 (1877); Jourdan, *ibid.*, **200**, 102 (1880); Böeseken and v. Senden, *Rec. trav. chim.*, **32**, 23 (1913).

(3) "Organic Syntheses," Coll. Vol. I, p. 298.

(4) Levene and Taylor, *J. Biol. Chem.*, **35**, 281 (1918).

(5) Schepss, *Ber.*, **46**, 2568 (1913).

(6) Skita and Meyer, *ibid.*, **45**, 3589 (1912).

(7) Carothers and Adams, THIS JOURNAL, **45**, 1077 (1923); **46**, 1682 (1924).

(8) Clemmensen, *Ber.*, **46**, 1843 (1913); Karvonen, *Acta. Chem. Fennica*, **3**, 101 (1930); *Chem. Abs.*, **25**, 2412 (1931).

(9) Kao and Chang, *J. Chinese Chem. Soc.*, **2**, 18 (1934).

(10) Riedel, German Patent 444,665.

(11) Braun and Manz, *Ber.*, **67B**, 1696 (1934).

(12) Fischer and Meyer, *Brennstoff-Chem.*, **12**, 226 (1931).

(13) Kao and Ma, *Sci. Repts. Natl. Tsing Hua Univ.*, (A), **1**, 129 (1932).

with a 30-ml. sample is shown in Fig. 1. The portion distilled over between 67–70° was repeatedly treated with concentrated sulfuric acid,[14] washed with water, and distilled over sodium. It showed the following physical constants: b. p. 69°; d^{20}_4 0.6580; $n^{20}D$ 1.3760 (pure n-hexane has the values:[15] b. p. 68.8°; d^{20}_4 0.65942; $n^{20}D$ 1.37506). Its molecular weight as determined by the Victor Meyer vapor density method is 87.4 (C_6H_{14} = 86.1). All these established the fact that this product is n-hexane. The portion distilled over at 174–177° showed the characteristic odor of high alcohols, and $n^{20}D$ 1.4232; it is unquestionably n-heptyl alcohol. As indicated by the distillation curve (Fig. 1), the presence of other products and unchanged heptaldehyde is only in negligible quantities.

Discussion

When benzaldehyde was hydrogenated in gas phase with nickel catalyst at 210–235°, Sabatier and Senderens[16] obtained benzene as well as toluene

$$C_6H_5CHO + 2H_2 \longrightarrow C_6H_5CH_3 + H_2O$$
$$C_6H_5CHO + H_2 \longrightarrow C_6H_6 + CO + H_2$$
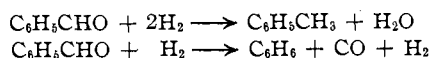
A part of the carbon monoxide formed was reduced to methane. With copper catalyst at 350°, the formation of benzene constituted the predominating reaction.[17]

With n-hexane and some n-heptyl alcohol as the main reaction products, the reactions encountered in the present investigation are evidently

$$C_6H_{13}CHO + H_2 \longrightarrow C_6H_{14} + CO + H_2$$
$$C_6H_{13}CHO + H_2 \longrightarrow C_6H_{13}CH_2OH$$
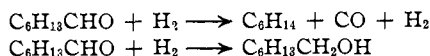
It must be noted, however, that in the case of benzaldehyde, toluene was obtained, but in the present case, no n-heptane was formed.

When the degradation reaction occurs, carbon monoxide is a necessary by-product. The gaseous products were therefore analyzed, which in average gave the following percentages:[18] CO_2 1.5, O_2 0.9, unsaturated compds. (absorbed in 87% sulfuric acid) 1.2, CO 22.0, H_2 51.5, CH_4 15.0, C_6H_{14} 1.3, and N_2 6.6 (by diff.). The presence of oxygen and nitrogen evidently is due to air leakage, while methane is undoubtedly a secondary product from carbon monoxide and hydrogen.

(14) The treatment of sulfuric acid gave an orange coloration. It is possible, though not probable, that the hydrocarbon and the alcohol form a constant boiling mixture. In "International Critical Tables," Vol. III, pp. 320–321, the following constant boiling mixtures of n-hexane and alcohols are listed, the figures being the mole % of the respective alcohols: ethyl alcohol 33.2, n-propyl alcohol 6, isobutyl alcohol 1. Judging from the trend, a constant boiling mixture of n-hexane and n-heptyl alcohol is not likely to form. The coloration was most probably due to a small amount of unsaturated hydrocarbons, which were also present in the gaseous products.

(15) Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Corp., New York, 1939, p. 36.

(16) Sabatier and Senderens, Compt. rend., 137, 301 (1903).

(17) Sabatier and Kubota, ibid., 172, 173 (1921).

(18) The percentages of methane and hexane are not very accurate.
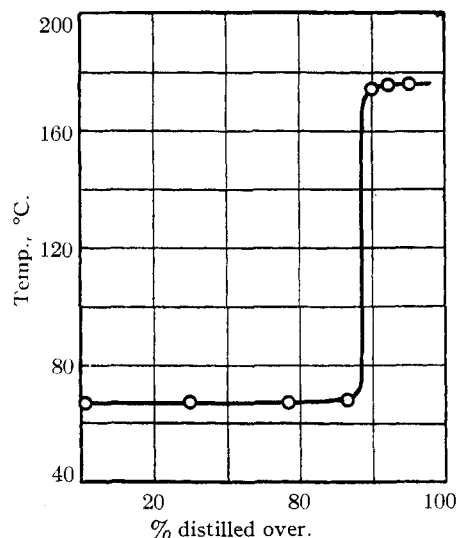
Fig. 1.—Fractionation of the anhydrous liquid product.

The data on analysis and percentage recovery are not accurate enough to allow a satisfactory material balance on the input and output. However, a rough check is possible. In one of the experiments, 0.37 mole of heptaldehyde was used, and the liquid product contained 0.27 mole of n-hexane and 0.07 mole of n-heptyl alcohol. The gases formed amounted to 18.7 liters (N. T. P.), which contained 0.32 mole of total carbon monoxide (including the secondary carbon dioxide and methane) versus 0.28 mole of n-hexane in both liquid and gaseous products. The amount of free hydrogen in the gaseous products plus that used up in forming methane and alcohol was 0.88 mole, while the actual amount used was 0.74 mole.

It is interesting to note that Böeseken and van Senden,[19] by passing n-heptyl alcohol at 220° over a finely divided nickel in a current of hydrogen, obtained 62% n-hexane, 17% of a mixture of heptyl alcohol and heptaldehyde. However, they stated that heptaldehyde is only slightly reduced by similar treatment, which is in direct contrast to this work. In their opinion, heptyl alcohol is first decomposed into hydrogen and heptaldehyde, which in turn decomposes into hydrogen, carbon monoxide and hexene-1. In a current of hydrogen, hexene is reduced to hexane. In the light of the present investigation, the reverse mechanism seems to be true. That is, heptaldehyde is first reduced to heptyl alcohol, which, by elimination of carbon monoxide and hydrogen, gave forth n-hexane. It is also possible that the reduction

(19) Böeseken and van Senden, Rec. trav. chim., 32, 23 (1913); Chem. Abs., 7, 1702 (1913).

and degradation are simultaneous reactions, taking place in parallel. The elucidation of the exact mechanism, however, requires further study.

Although not yet experimentally tested, the authors believe that this degradation reaction should be a general one for aliphatic aldehydes. Further work on this point is also desirable.

Summary

Heptaldehyde was hydrogenated with a nickel catalyst at 250° under atmospheric pressure. A degradation reaction was observed. The main product was found to be n-hexane, some n-heptyl alcohol also being obtained. The carbon monoxide formed was partially reduced to methane.

The Rate of Reduction of Vanadium Pentoxide in Concentrated Acid Solutions. Reduction of Vanadium Pentoxide by Arsenious Acid, Oxalic Acid, Formaldehyde and Ethyl Alcohol*

By M. Bobtelsky and A. Glasner

Pentavalent vanadium can be reduced to the tetravalent stage by many reducing agents almost all of which react only in acid solutions. The literature on this subject is rather poor,[1,2,3] since it deals primarily with analytical questions. The aim of this article is to present a preliminary study of the reduction of pentavalent vanadium by four different reducing agents.

1. **Experimental.**—The solutions for the experiments were made up in small glass-stoppered flasks kept in a thermostat. In all experiments a $^2/_3$ M solution of Na-VO$_3$·4H$_2$O (Merck) was used. The total volume of the reacting solutions was always 20 cc., reduced to a minimum because we were working in highly concentrated solutions. Solutions containing sulfuric acid were prepared from concentrated acid (96%) by calculating the contraction of sulfuric acid solutions from tables in Landolt and Börnstein. A few experimental controls have shown that the difference between the calculated and real volumes never amounted to more than 1%. The reducing agent always was introduced in a large excess, at least five times above the amount necessary for a complete reduction of pentavalent to tetravalent vanadium. The thermostat was kept at a constant temperature of 30° (±0.1°), unless otherwise stated. The time of reaction was counted from the moment the last reagent was introduced into the flask. At known intervals 2 cc. of the solution was pipetted out with precise micropipets into 13 cc. of distilled water, thus diluting the solution and greatly reducing the velocity of the reaction, even stopping it altogether. The extinction of a 50-mm. column of the diluted solution was measured with a Hellige panphotometer, equipped with colored filters at the approximate wave lengths of 660 and 690 mμ.

(The two measurements served as a control for each other, giving good agreement; they gave a maximum difference of 2%.) The extinction thus measured was proportional to the concentration of blue tetravalent vanadium (as we ascertained in a large number of various acid solutions). The reacting solutions were originally yellow-orange to red color (depending predominantly on the acid concentration), turned green with time (even a small amount of vanadium pentoxide in a highly concentrated acid solution of tetravalent vanadium imparted a green color to the solution) and occasionally showed a very dark appearance. Two cc. of the dark green solution gave a blue color when diluted with 13 cc. of water. After the reduction was complete (from a day or two up to a week) the reacting solution had a blue-violet color.

2. **Reduction of Vanadium Pentoxide with Arsenious Acid.**—Various compounds of vanadium pentoxide and arsenic pentoxide have been known since Berzelius. Since then many have worked on these compounds, but very few have even as much as mentioned that vanadium pentoxide was reduced by arsenious oxide under certain conditions.[4,5,6]

For the preparation of solutions containing various amounts of arsenious oxide, a stock solution of 1 M arsenious oxide in 5.16 N sodium hydroxide was used. In order to study the influence of strong acids on the velocity of the reduction, two series of experiments with hydrochloric and sulfuric acids were made. The reaction solutions in each experiment contained 3 cc. of $^2/_3$ M NaVO$_3$ + 2.5 (or 5) cc. of As$_2$O$_3$ + x cc. of acid; the total volume was 20 cc. In all experiments with arsenious acid, on calculating the final concentration of the acid an appropriate correction for the sodium hydroxide in the arsenious oxide solution was applied, but no correction for arsenious or vanadic acid was made. The vanadium was clearly reduced by arsenious acid at a measurable rate (in contradiction to R. Lang[6]). The results are given in Table I.

* Original manuscript received May 9, 1941.

(1) M. Bobtelsky and S. Czosnek, *Z. anorg. allgem. Chem.*, **205**, 401–13; **206**, 113–24 (1932).

(2) M. Bobtelsky and L. Chajkin, *ibid.*, **209**, 95–104 (1932).

(3) E. F. Krauze and O. I. Vorobieva, *Sci. Rep. Moscow State Univ.*, No. 6, 5–13 (1936).

(4) A. Ditte, *Compt. rend.*, **101**, 1487 (1885).

(5) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IX, p. 199.

(6) R. Lang, *Z. anorg. allgem. Chem.*, **152**, 205 (1926).