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Hydrogenation of Isobutylene Under Atmospheric Pressure.

By

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INTRODUCTION.

It is very often necessary for research chemists who deal with hydrocarbon chemistry to obtain a certain hydrocarbon in its pure state. Preparation of pure hydrocarbons is in itself a difficult problem especially in the case of the higher homologues. The most easily obtainable pure hydrocarbons may be gaseous olefins, such as ethylene, propylene, normal butylene and isobutylene. They are prepared by dehydration of the corresponding alcohols, viz., ethylene from ethyl alcohol, propylene from normal or iso-propyl alcohol, normal butylene from normal butyl alcohol, and isobutylene from tertiary or iso-butyl alcohol, in the presence of dehydration catalysts. The dehydration catalysts conventionally used are alumina, kaolin, acid clay, sulfuric acid, phosphorus pentoxide, anhydrous oxalic acid, etc. But those catalysts which may cause isomerization of the product hydrocarbons under dehydrating conditions must be avoided.

Paraffin hydrocarbon gases require more complex steps for their preparation as compared with olefin gases. Paraffin gases are generally prepared by decomposition of the corresponding alkyl halides. But this procedure is rather troublesome.

The author found that heavy paraffin gases, such as propane or butanes, are easily prepared in good yield by catalytic hydrogenation of the corresponding olefins under atmospheric pressure. As an example, hydrogenation of isobutylene to produce isobutane is reported in the following.

EXPERIMENTAL.

Sample. Isobutylene was prepared by dehydration of pure isobutyl alcohol at ca. 400 deg. C. in the presence of kaolin. Isobutylene thus produced contained a small amount of normal butylene. For hydrogenation of isobutylene, commercial bottled hydrogen was used.

Hydrogenation Catalysts.

Nickel Catalyst. Two hundred and fifty g. of nickel nitrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was heated in a porcelain dish until it dissolved in its crystal water. Seventy g. of pumice stone was then added into the solution and impregnated with the nickel nitrate by evaporating the solution with constant stirring. The nickel

nitrate adsorbed on pumice was changed to nickel oxide by calcining the catalyst mass at ca. 450 deg. C. The catalyst charged in the reaction tube was treated with hydrogen stream at ca. 350 deg. C. before use. Hence, the nickel in the catalyst ready for use was in the form of reduced metal.

Molybdenum Catalyst. Ammonical solution of ammonium thiomolybdate containing 1 kg. of this reagent was first saturated with hydrogen sulfide. One and half kg. of pumice stone was then added into the sulfurized solution and impregnated with the thiomolybdate by evaporating the solution with constant stirring.

Apparatus and Procedure.

Atmospheric hydrogenation of isobutylene was conducted in the apparatus shown in Fig. 1. The mixture of isobutylene and hydrogen (50:50 in volume) contained in the gas holder (1) was charged into the reaction tube (5) at a constant rate of flow. The product gases were collected in the gas holder (2). The reaction tube contained 35 g. of catalyst for each experiment. Diameter of the

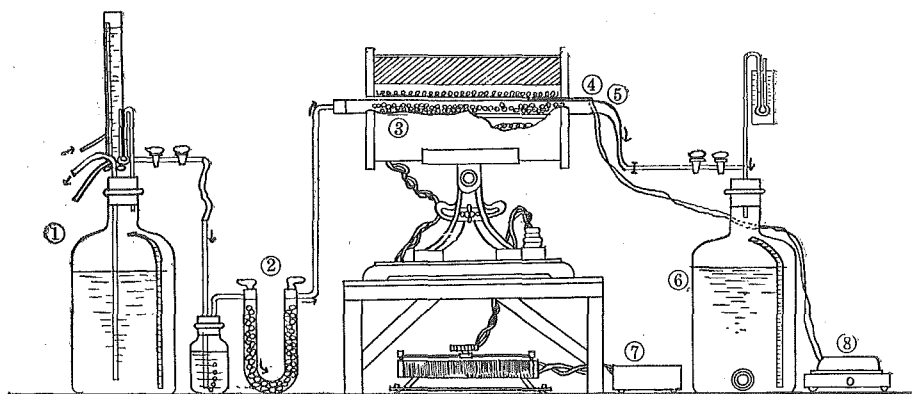


Fig. 1. Diagram of the Apparatus.

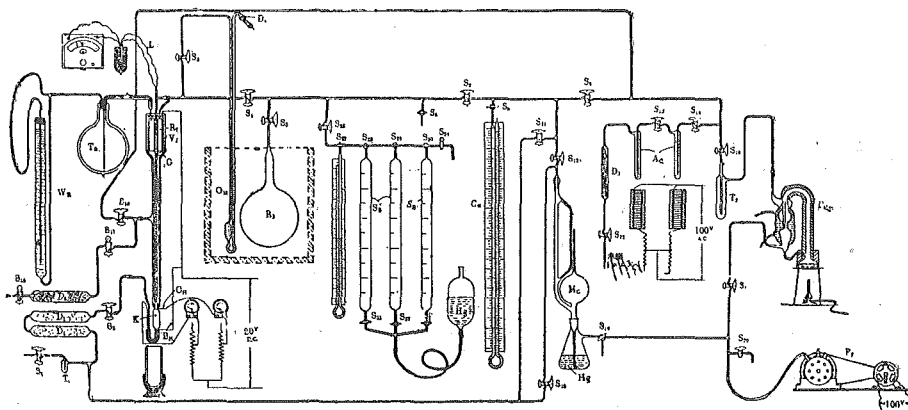


Fig. 2. Low Temperature Fractionation Apparatus.

reaction tube was 2 cm. and the volume occupied by the catalysts was 114 c.c. for nickel catalyst and 57 c.c. for molybdenum catalyst. The product gases were analyzed by the Podbielniak apparatus modified by the author as shown in Fig. 2.

Experimental Results.

Results of the hydrogenation experiments are summarized in the following tables.

Table 1. Reaction Conditions.

Exp. No.	5	12	16	17
Sample gas mixture (l. at N. T. P.)	9.77	9.62	9.85	9.75
i-C ₄ H ₈ vol. in sample gas (l. at N. T. P.) . .	4.78	4.79	4.82	4.71
React. temp. (°C.)	350	300	300	250
Catalyst	Ni	Ni	Mo	Ni
Rate of flow (c.c./min.)	31	31	31	31

Table 2. Yield of Reaction Products.

Exp. No.	5	12	16	17
React. temp. (°C.)	350	300	300	250
Vol. of gaseous products (l.)	8.48	5.52	8.71	5.27
Vol. of condensible gas at -80°C (l.) . . .	4.41	4.56	2.66	3.97
Vol. of i-C ₄ H ₁₀ produced (l.)	1.94	3.67	0.41	2.55
Vol. of unchanged i-C ₄ H ₈ (l.)	2.48	0.89	2.25	1.42
Conversion per pass	48.3	81.4	58.3	69.8
Yield of i-C ₄ H ₁₀ (%)	40.7	71.6	8.5	54.1

Table 3. Analysis of Gaseous Products by Low Temperature Distillation.

Exp. No.	5	12	16	17
Vol. of gaseous products (l.)	8.48	5.52	8.71	5.28
H ₂ with small amount of N ₂ (%)	—	12.8	69.3	24.6
C ₄ -Hydrocarbons (%)	—	4.3	0	0
C ₃ -Hydrocarbons (%)	—	0	0	0
Unreacted i-C ₄ H ₈ (%)	—	16.3	25.9	27.0
i-C ₄ H ₁₀ produced (%)	—	66.6	4.8	48.4

Low temperature distillation curve of the gaseous products in Exp. 12 is shown in Fig. 3.

Observations on the Results.

Hydrogenation of isobutylene to produce isobutane was successfully conducted under atmospheric pressure and at 350 deg. C. in the presence of nickel catalyst.

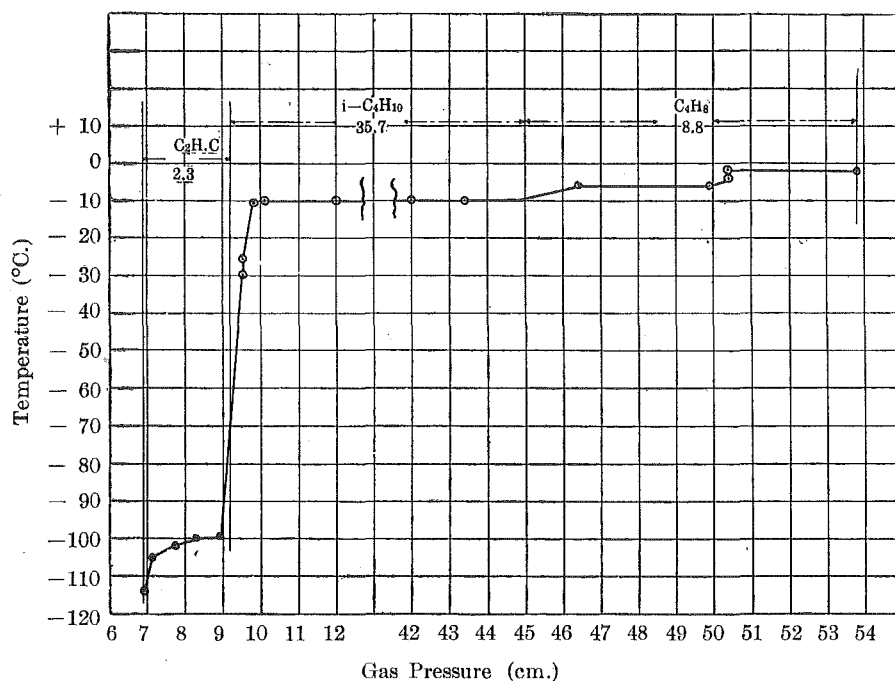


Fig. 3. Low Temperature Fractionation Curve. (Exp. 12)

Under these conditions, over 70% of the isobutylene was converted to isobutane. Pure isobutane was easily obtained by fractionation of the hydrogenated products followed by 87% sulfuric acid washing.

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