

Chemistry. — “*Researches on the Addition of Water to Ethylene and Propylene*”. (Preliminary Communication). By Dr. J. P. WIBAUT and J. J. DIEKMANN. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated at the meeting of March 24, 1923).

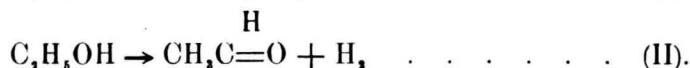
About two years ago experiments were carried out by one of us purposing to study the possibility of a direct addition of water to ethylene and propylene. The continuation of this investigation has been rendered possible by a liberal support granted me from the HOOGEWERFF-fund. I gladly avail myself of this opportunity to express my great indebtedness to the Board of Management of the HOOGEWERFF-fund for this help.

Though these investigations have not yet been completed, it seems desirable to me in connection with a short notice in the „Chemiker Zeitung” of Jan. 2nd 1923 (N^o. 47, p. 7), in which H. W. KLEVER describes similar researches, to publish a preliminary communication on the results obtained by us.

J. P. WIBAUT.

§ 1. *The Action of Water-vapour on Ethylene and Propylene in the Presence of Catalysts.*

Since the investigations by IPATIEW, SENDERENS and SABATIER it has been known that at high temperature and in the gaseous condition ethyl-alcohol and some of its homologues can be decomposed in two ways:



Both reactions are typical catalytic reactions, which only proceed readily in the presence of certain contact-substances. Anhydrous aluminiumsulphate and aluminiumoxide are typical catalysts that split off water (reaction I). Metals like copper and iron, especially in finely divided condition, are typical catalysts for the splitting off of hydrogen (reaction II).

The range of temperature, in which particularly the first reaction

takes place, lies between 300—400°, dependent on the nature of the catalysing substance; when the temperature is raised to about 400° and higher, the formation of aldehyde becomes prominent even in the presence of substances like aluminium oxide and other catalysts that split off water.

It is well known that reaction (II) is reversible — aldehydes can be smoothly reduced with molecular hydrogen over nickel — but nothing is known about the reversibility of reaction (I).

In the extensive literature on the splitting up of alcohols into olefine and water, the question whether direct addition of water to the double bond in ethylene and propylene is actually possible, has never been examined. We have carried out a number of experiments to answer this question. A mixture of ethylene and water-vapour was led over different contact-substances at a temperature between 300° and 400° C. On use of aluminiumhydroxyde or of aluminium sulphate as catalysts, the reaction product contained acetaldehyde. We have proved the presence of acetaldehyde by the usual reactions (reduction of an ammoniacal solution of silver hydroxide); SCHIFF'S reaction; reaction with nitro-prussidsodium and piperidine according to LEWIN) and also isolated as p-nitrophenylhydrazone. The quantities of acetaldehyde are very small; by far the greater part of the ethylene remains unchanged during the experiment. The quantity of acetaldehyde amounted to from 0,2 to 0,4 % at 350°—360°, calculated to the quantity of ethylene.

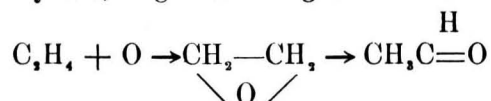
The presence of alcohol could not be verified ¹⁾).

In our opinion the formation of acetaldehyde must be explained in this way that primarily ethylalcohol is formed through addition of water to ethylene, and then acetaldehyde through splitting up of hydrogen. If this second reaction proceeds much more rapidly than the addition of water to the double bond, no alcohol will be found in the reaction product. As at 350°—360° ethyl-alcohol is almost quantitatively decomposed into ethylene and water (at this temperature, however, a little hydrogen is also formed) it is clear that only at a lower temperature the inverse reaction can take place in a considerable degree. We have, however, not succeeded in finding a catalyst that causes the addition of water to ethylene below 300°.

We have proved by means of a separate experiment that no acetaldehyde is formed from mixtures of dry ethylene with about 10% of air at 360° over aluminiumoxide. It, therefore, appears from

¹⁾ The analytical particulars will be given later, as also the full description of the arrangement of the experiments.

this that the formation of acetaldehyde is not the consequence of an oxidation of ethylene, e. g. according to the scheme



Hence the formation of acetaldehyde cannot have been caused by the possible presence of small quantities of air in the ethylene used.

We are, therefore, of opinion that we are justified in concluding that a primary addition of water to the double bond has taken place, and that the reaction:



may accordingly be considered as a reversible reaction.

We have obtained perfectly analogous results with mixtures of propylene and water-vapour. At 350° and in the presence of aluminiumhydroxide *acetone* was then formed in a quantity of from 0,2 to 0,3 % of the propylene. In our opinion the primary formation of isopropylalcohol by addition of water to propylene, must be assumed in this case. Afterwards the isopropylalcohol is transformed to acetone through the splitting off of hydrogen. Hence the direct addition of water proceeds analogously to the addition of hydriodic acid, in which likewise the isopropyl compound appears. Accordingly the rule of MARKONIKOW remains valid also in this case.

On the ground of these results it is probable that the addition of water to propylene and ethylene can take place under high pressure at temperatures far below 300°. We have, however, made no experiments in this direction.

§ 2. *The Hydration of Ethylene and Propylene by Means of Acids.*

The syntheses of ethyl- and isopropylalcohol from ethylene and propylene by the formation of alkyl-sulphuric acid, and subsequent hydrolysis, by M. BERTHELOT¹⁾ are among the classic syntheses of organic chemistry. BERTHELOT investigated the absorption of these olefines by pure sulphuric acid of 98—99 % H₂SO₄ at ordinary temperature. Afterwards the absorption of ethylene by sulphuric acid has been repeatedly studied. Particularly in the last few years several technical chemists have made experiments to absorb the ethylene from

¹⁾ BERTHELOT: Chimie organique fondée sur la synthèse, p. 115. c. f. Ann. de Chimie et de Physique. (7), 4, 101 (1895). Bull. Soc. Chim. XI, 13. (1869).

coal-distillation gases by means of hot strong sulphuric acid (of 96 %), and to obtain ethylalcohol after dilution and distillation of the sulphuric acid ¹⁾.

With regard to the action of sulphuric acid on propylene, a process of CARLETON-ELLIS ²⁾ has become known. In this process the waste gases formed in the preparation of light hydrocarbons from heavy petroleum-distillates (cracking-process of BURTON) are passed through sulphuric acid of 87 %; the propylene present in these is said to be transformed into isopropylsulphuric acid. After dilution and distillation of the sulphuric acid isopropylalcohol is obtained.

Systematic researches on the behaviour of ethylene and propylene towards acids of different concentrations have not been published.

On the other hand there are many instances known, in which the addition of water to a double bond takes place under the influence of diluted acids. Geraniol absorbs two molecules of water when treated with 5 % sulphuric acid. BUTLEROW ³⁾ found that isobutylene and heptylene were very slowly hydrated to the corresponding alcohols by means of diluted sulphuric acid and nitric acid at the ordinary temperature.

It seemed interesting to us to examine how ethylene and propylene would behave towards acids of different concentrations. If ethylsulphuric acid can be obtained through the action of ethylene on diluted sulphuric acid at high temperature, there would be a possibility that afterwards the ethylsulphuric acid should be hydrolyzed:



If the two reactions proceeded rapidly enough, the experiment might be arranged so that the alcohol formed is immediately distilled off from the reaction liquid.

Such a course of the reaction would then be practically an addition of water to ethylene, in which the question whether we have to do here with a direct addition or which an intermediary

¹⁾ FRITZSCHE. *Chemische Industrie* **20**, 266 (1897) and **21**, 27 (1898); TAU and BERTELSMANN, *Glück Auf* **57**, 189 (1921); BURY en OLLANDER: „Byproduct development in the Iron and Steel Industry”; Paper read before the Cleveland Institution of Engineers, 15 December 1919; cf. TIDMAN, *Journ. Soc. Chem Ind.* **40**, 86 T (1921); DE LOISY. *Compt. Rend. Ac. d. Sc. Paris* **170**, 50 (1920); DAMIENS, DE LOISY en PIETTE, *Eng. Pat.* 180988 (1922).

²⁾ Cf. *Chemical and Metallurgical Engineering*. Vol. **23**, 1230 (1920).

³⁾ *Lieb. Ann.* **180**, 245 (1876).

formation of ethylsulphuric acid, can be left undecided for the present.

We have devised an apparatus, in which an ascending stream of gas came into intimate contact with the descending acid. This washing apparatus, which is placed vertically was electrically heated by means of a coil of nichrome-wire so as to make it possible to keep the reaction temperature constant within narrow limits. The ethylene, which is led through the heated, diluted sulphuric acid will withdraw water-vapour from the liquid, for so far as it is not absorbed, which would cause the acid to become more concentrated in the course of the experiment. To prevent this we have added water-vapour to it at the same time with the ethylene; the partial tension of the water-vapour in the introduced gas-mixture was about the same as the water-vapour tension of the used sulphuric acid at the temperature of the experiment. In this way the concentration of the sulphuric acid was kept about constant during the experiment.

At the top of the apparatus there escaped, therefore, water-vapour, not absorbed ethylene, and alcohol vapour, if any was formed.

It actually appeared possible to obtain alcohol from ethylene in this way. A mixture of ethylene and steam was washed with sulphuric acid of 65 % H_2SO_4 at a temperature of 150° — 160° . After 5 litres of ethylene had been passed through in 5 hours' time, the distillate contained 0,21 gr. of alcohol¹⁾, i. e. a conversion of about 2 %.

Then the sulphuric acid used was strongly diluted and distilled out, and in this way 0,08 gr. of alcohol more was obtained. Hence a little ethylsulphuric acid was still present in the sulphuric acid after the experiment. This renders it probable that the ethylsulphuric acid is formed as an intermediate product, and that accordingly the formation of alcohol is the result of two successive reactions, as given above.

In a second similar experiment 4 % of the ethylene that was passed through, was converted into ethylalcohol.

With a mixture of sulphuric acid and water containing 55% H_2SO_4 only 0.01 gramme of ethylalcohol was found in the distillate, when 5 litres of ethylene mixed with steam had been passed through at 140° .

With sulphuric acid of 70 %, no alcohol was found in the distillate, when three litres of ethylene had been passed through. After

¹⁾ The analysis took place by oxidizing the reaction liquid with chromic acid, in consequence of which the alcohol present was oxidized to acetaldehyde. This latter was determined colorimetrically.

dilution and distillation the sulphuric acid yielded, however, 0.32 gr. of alcohol, which was, therefore, present as ethylsulphuric acid. This corresponds with a conversion of 5 %.

In these experiments most of the ethylene passed unchanged through the sulphuric acid; only a slight carbonisation took place. Though in principle it, therefore, appears possible to convert ethylene in this way into ethylalcohol, the yield was so small that no practical significance can be assigned to these experiments.

These researches are being continued with other acids and with salts, as aluminiumsulphate and others.

§ 3. *Propylene and Sulphuric Acid.*

It is well known from BERTHELOT's investigations that propylene is very rapidly absorbed at the ordinary temperature by sulphuric acid of 98—99 %. We have first of all made some preliminary experiments on the action of sulphuric acid of different concentrations on propylene.

In a HEMPEL's gas-pipette 100 cc propylene was placed together with the sulphuric acid to be examined.

Sulphuric acid of 96 % at once absorbs the propylene, also sulphuric acid of 90 % acts very rapidly on it; with acid of 85 % the propylene is absorbed after 20 minutes' shaking, about an hour being required for this with acid of 80 %. Also sulphuric acid of 75 % still absorbs propylene, but very slowly.

We have further investigated the action of propylene on sulphuric acid of 96 % at 0°, in which we carefully guarded against rise of temperature both during the absorption of the gas, and during the pouring out of the reaction product on ice. We have only succeeded in obtaining a small quantity of isopropylalcohol from the reaction product.

Through the action of the sulphuric acid the bulk of the propylene was changed into an oily liquid, which was unsaturated, and boiled within wide limits. It is, therefore, probable that higher unsaturated hydro-carbons are formed by the condensing action of the sulphuric acid. BERTHELOT too states that such condensation products are formed, when rise of temperature takes place during the experiment. In our experiments with sulphuric acid of 96 % at 0° the bulk of the propylene was always transformed into condensed and resinous products in spite of all our precautions. With sulphuric acid of 85 %, the absorption of propylene takes place very slowly at 10°. On further treatment

of the reaction product, chiefly condensation products were again obtained.

We then examined the absorption of propylene by more diluted sulphuric acid at higher temperature. The experiments were arranged in the same way as was already described for ethylene. The mixture of propylene and steam was brought in contact in counter-current with sulphuric acid of definite concentration and definite temperature in the vertical washing-apparatus; 7.5 litres of propylene mixed with steam were passed in 4 hours through sulphuric acid of 55 % H_2SO_4 at 140° . The distillate contained 0.25 gr. isopropyl alcohol. After dilution with water a distillate was obtained from the acid in which 0.27 gr. of isopropylalcohol¹⁾ was present. There was, therefore, evidently still isopropylsulphuric acid present in the acid. In all 2.6 % of the total quantity of propylene was, accordingly, obtained as isopropyl alcohol.

A much greater part of the propylene was, however, decomposed. Separation of carbon took place and formation of sulphur-dioxide. After the experiment 5,3 litres of the 7,5 litres of propylene was found back. Hence 9 % of the consumed quantity of propylene was changed into isopropyl alcohol.

An experiment with sulphuric acid of 45 % H_2SO_4 and at $125-130^\circ$ proceeded in the same way; 6 litres of propylene were passed through, 5 litres of them were obtained after the experiment. The yield of isopropyl alcohol amounted to 0,2 gramme in the distillate and 0.1 gramme in the acid liquid, together 0,30 gr. i.e. 10 % of the consumed propylene. Here too a large part of the consumed propylene was carbonised.

It therefore, appears from these experiments that the hydration of propylene by hot diluted sulphuric acid is possible. The reaction velocity, however, is small, which renders the yield small. Besides the sulphuric acid has a decomposing action on the propylene. If on the other hand the experiment is made with concentrated sulphuric acid at low temperature, the propylene is quickly attacked, but chiefly transformed into condensation products.

We have tried therefore the action of other acids. We first investigated the action of benzene sulphonic acid. 6 litres of propylene with steam were passed through a concentrated solution of benzene sulphonic acid; in the aqueous distillate of this experiment we found 0,25 gr. isopropyl alcohol or about $1\frac{1}{2}$ % of the propylene. Hence in this case too the reaction proceeds slowly.

¹⁾ The analysis took place by oxidation to acetone, and colorimetric determination of this substance.

The result of the experiments on the action of acids on ethylene and propylene can, therefore, be summarized as follows: It is possible to obtain ethyl alcohol, resp. isopropyl alcohol by one operation from ethylene and propylene by means of mixtures of sulphuric acid and water at 130–150°. In this reactions the alkylsulphuric acids are probably formed as intermediate products.

The yield of alcohols is, however, very small, and particularly with propylene, the hydro-carbon is decomposed in another way during the experiment. These investigations are being continued.
