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STUDIES ON ETHINYLATION REACTIONS, II

Synthesis of Propargyl Alcohol

By Keizo Suzuki

Introduction

Propargyl alcohol is usually produced as the intermediate when butynediol-1, 4 is synthesized from acetylene and formaldehyde, but it is to be possible to obtain propargyl alcohol as the main product if the conversion to butynediol can be checked by controlling suitably the reaction conditions. W. Reppe\textsuperscript{1} has obtained the satisfactory results in the synthesis of propargyl alcohol in a continuous process, while the unsuccessful result has been reported so far as a continuous process is adopted\textsuperscript{2}. Therefore, it is expected that the synthesis of propargyl alcohol as the main product is difficult in comparison with the case of butynediol.

From the previous studies on the kinetics of the reaction of acetylene with aqueous formaldehyde solution\textsuperscript{3,4} and the synthesis of butynediol in a continuous process\textsuperscript{5}, the results of the investigations on the propargyl alcohol synthesis are summarized as follows. The rate, the apparent equilibrium concentration of propargyl alcohol and the ratio in moles of the quantity of the propargyl alcohol formed to that of formaldehyde consumed, $P/F$ increase when acetylene pressure is raised. In the cases where pH is low and the methanol content contained in an aqueous formaldehyde solution is high, the concentration of propargyl alcohol formed and $P/F$ come to exceed the cases where pH is high and the methanol content is low, though the reaction rate is slow at the earlier stage. The rate of propargyl alcohol formation increases with the elevation of the reaction temperature and the initial formaldehyde concentration, but $P/F$ inversely decreases.

From the summarized results it is found that to raise acetylene pressure is a good condition in the propargyl alcohol synthesis without exception in considering the formation rate, the apparent equilibrium concentration and $P/F$. However, the pressure of about 40 kg/cm\textsuperscript{2} which was used in the previous report\textsuperscript{4} is a limit from the consideration of the state diagram\textsuperscript{6}. Then, it is considered to use such a suitable solvent...

\textsuperscript{1} J. W. Copenhaver and M. H. Bigelow, Acetylene and Carbon Monoxide Chemistry, p. 105 (1949)
\textsuperscript{2} G. M. Klein, Mod. Plast., Feb. 71 (1946)
\textsuperscript{3} R. Kiyama, J. Osugi and K. Suzuki, This Journal, 22, 22 (1952)
\textsuperscript{4} R. Kiyama, J. Osugi and K. Suzuki, ibid., 22, 59 (1952)
\textsuperscript{5} K. Suzuki, ibid., 23, 57 (1953)
\textsuperscript{6} R. Kiyama, T. Ikegami and K. Inoue, ibid., 21, 58 (1951)
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of acetylene that the same effect as the elevation of pressure may be brought about. It seems that a good result which was obtained in large methanol content depends on the solvent effect of methanol for acetylene gas.

It is not easy to remove the residual formaldehyde, and so it is necessary to make the quantity of its residual small by the reaction. This point has to be considered in the selection of the reaction condition.

Referring to the summarized results of the previous reports, the experimental results of the propargyl alcohol synthesis obtained in a continuous process, where tetrahydrofuran is used as a solvent, is reported here.

Moreover, the results of a solvent effect of tetrahydrofuran, methanol and acetone, and other results obtained in a static method are added.

Experimental

(1) Continuous process

The experimental apparatus and its procedures are the same as in the previous report. The copper acetylide catalyst which was already used for about 200 hours in the previous work is used in succession.

The liquid sample used is prepared by adding a given quantity of tetrahydrofuran to about 40% aqueous formaldehyde solution obtained by dissolving paraformaldehyde in a distilled water by boiling, where a small quantity of sodium hydroxide is used in order to make dissolution easy. The pH of the sample is controlled with sulphuric acid and sodium hydroxide to a given value.

The analyses are the same as in the previous report, but the analysis of butynediol by the addition method of bromine can not be used in this experiment, because it is difficult to determine the end point in the iodometry due to the presence of tetrahydrofuran. Therefore, the concentration of the butynediol formed is calculated stoichiometrically from the concentrations of the formaldehyde decreased and the propargyl alcohol formed.

(2) Static method

The experimental procedures of the static method is the same as in the previous report. Tetrahydrofuran, methanol and acetone are used as a solvent. The sample is prepared for methanol from a commercial formaldehyde solution, and for acetone from an aqueous formaldehyde solution prepared from paraformaldehyde respectively.

Experimental Results

(1) Continuous process

* The sample is prepared from paraformaldehyde instead of using a commercial aqueous formaldehyde solution, because the separation of tetrahydrofuran from the methanol contained in its solution is difficult. The solubility of paraformaldehyde in tetrahydrofuran being about 2%, water is used as a solvent in the preparation of the sample, though it is not desirable to use water from the reason that the separation of propargyl alcohol from water is difficult.
Experimental conditions: 15, 20 kg/cm² pressures, 110, 120°C as the reaction temperatures, and 0.7 ~ 1.5 l/l hr and 1.3 ~ 2.0 l/l hr in the space velocities, S.V. of liquid and gas respectively. The effects of pressure, temperature, tetrahydrofuran content and pH on the reaction are investigated, and the relations of the concentrations of the formaldehyde decreased, the propargyl alcohol and butynediol formed against the reciprocal of the space velocity of the liquid sample, 1/S. V. (or the contact time, hour) are obtained.

In order to summarize the results and discuss the excellence in the synthetic condition of propargyl alcohol, the values of Tr, Pr, (P/F)r and (S. T. Y.)r obtained from the experimental results are shown in Table 1. As the separation of the formaldehyde

<table>
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<tr>
<th>Exp. No.</th>
<th>Temperature (°C)</th>
<th>Pressure (kg/cm²)</th>
<th>Liquid sample</th>
<th>HCHO (g/100 cc)</th>
<th>F/HO</th>
<th>P, T.H. F.</th>
<th>pH</th>
<th>Tr (1/hr)</th>
<th>Pr (g/100 cc)</th>
<th>(P/F)r (g/l)</th>
<th>(S. T. Y.)r (g/l hr)</th>
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<tr>
<td>P 1</td>
<td>120</td>
<td>20</td>
<td></td>
<td>10.0</td>
<td>1/1</td>
<td>4.7</td>
<td></td>
<td>3.82</td>
<td>5.9</td>
<td>20.1</td>
<td>15.5</td>
</tr>
<tr>
<td>P 3</td>
<td>110</td>
<td>20</td>
<td></td>
<td>11.3</td>
<td>1/2</td>
<td>4.7</td>
<td></td>
<td>3.82</td>
<td>5.9</td>
<td>20.1</td>
<td>15.5</td>
</tr>
<tr>
<td>P 4</td>
<td>110</td>
<td>15</td>
<td></td>
<td>9.8</td>
<td>1/3</td>
<td>3.1</td>
<td></td>
<td>3.82</td>
<td>5.9</td>
<td>20.1</td>
<td>15.5</td>
</tr>
<tr>
<td>P 7</td>
<td>110</td>
<td></td>
<td></td>
<td>11.3</td>
<td>1/2</td>
<td>4.7</td>
<td></td>
<td>3.82</td>
<td>5.9</td>
<td>20.1</td>
<td>15.5</td>
</tr>
<tr>
<td>P 9</td>
<td>110</td>
<td>20</td>
<td></td>
<td>10.0</td>
<td>1/1</td>
<td>4.7</td>
<td></td>
<td>3.82</td>
<td>5.9</td>
<td>20.1</td>
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Notes
F/T.H. F.: Volume ratio of aqueous formaldehyde solution to tetrahydrofuran.
P: Concentration (g/100 cc) of propargyl alcohol formed at Tr.
(P/F)r: Percentage of ratio in moles of the propargyl alcohol formed to the formaldehyde consumed at Tr.
(S. T. Y.)r: Space time yield of propargyl alcohol at Tr.

residual in the reaction products is not easy, it is necessary to decrease its concentration without interfering with the separation of propargyl alcohol. Tr denotes the contact time required to reach a definite final concentration of formaldehyde, which is taken as 0.3 g/100 cc for convenience according to W. Repp. The values are obtained by extrapolation of the experimental results except Exp. No. P 3, and the method is described in the section of kinetical considerations. The synthetic condition where both the values of (P/F)r and (S. T. Y.)r are large is superior.

(a) Pressure effect

From the comparison between Exp. Nos. P 3 (20 kg/cm²) and P 4 (15 kg/cm²), it is clear that the case where the pressure is higher is the better condition for the propargyl alcohol synthesis.

(b) Temperature effect

In the comparison between Exp. Nos. P 9 (120°C) and P 10 (110°C), (S. T. Y.)r is larger in the former, but (P/F)r in the latter. Accordingly, in order to synthesize propargyl alcohol as the main product, the large value of (P/F)r at the low temperature should be selected though (S. T. Y.)r is small. However, if the butynediol formation is allowed to
a certain extent, the large value of \((S.\ T.\ Y.)_t\) at the high temperature should be selected.

(c) Effect of tetrahydrofuran content

As the formaldehyde concentration decreases with the increase of the solvent, the effect of the concentration is also included in these results. In the cases where the values of \(F/T.\ H.\ F.\) are 1/1 and 1/2, from the comparison between Exp. Nos. P 1 (1/1) and P 3 (1/2), the values of \((P/F)r\) and \((S.\ T.\ Y.)_t\) are remarkably larger in the latter. When the values of \(F/T.\ H.\ F.\) are 1/2 and 1/3, from the comparison between Exp. Nos. P 9 (1/2) and P 7 (1/3), the effect of the solvent increase is recognized. Though the effect is not so distinguished as in the former case, there is the advantage in the separation of propargyl alcohol, if the quantity of the solvent used is large.

(d) pH effect

In the cases of pH 4.7 and 3.1, from the comparison between Exp. Nos. P 4 (4.7) and P 9 (3.1), \((P/F)r\) is slightly larger in the latter, but \((S.\ T.\ Y.)_t\) considerably larger in the former. Therefore the case of pH 4.7 is superior as the synthetic condition.

(2) Static method

Experimental conditions: 30 kg/cm\(^2\) pressure, 105°C as a reaction temperature, and 1.0 ~ 1.3 l/hr in S.V. of gas. The results on the effect of the solvent and pH on the reaction are shown in Figs. 1 and 2, where the concentrations of the formaldehyde decreased, the propargyl alcohol and butynediol formed are plotted against the reaction time.

In these results obtained in the static method the longer reaction time being necessary to complete the reaction, it is difficult to discuss the results as in the continuous process. In this case, therefore, from the reaction curves in Figs. 1 and 2 the percentage of ratio in moles of the propargyl alcohol formed to the formaldehyde consumed at 4 hours \((P/F)_t\) is discussed from the standpoint of the synthetic condition. The experimental conditions are noted respectively in the figures.
(a) Solvent effect

The values of $(P/F)$, become large in order of 47.7% in tetrahydrofuran, 49.1% in acetone and 54.2% in methanol, but the reaction rate is remarkably slow in methanol in comparison with the other two. The reaction rate in acetone is larger than the case of tetrahydrofuran in the earlier stage of the reaction, but with the lapse of the reaction time the latter comes to exceed the former, and therefore it seems that tetrahydrofuran is most excellent among these three as a solvent.

(b) pH effect

In pH 3.1 and 2.1 the reaction rate as a whole (i.e. the rate of formaldehyde decrease) is smaller in the latter, but the values of $(P/F)_4$ are 47.7 and 55.6% respectively, and the rate of propargyl alcohol formation, moreover, being linear with the lapse of the reaction time in comparison with the former, such a tendency as the quantity of propargyl alcohol formed comes to be superior to the former is found*. Accordingly, in order to synthesize propargyl alcohol as the main product the case of pH 2.1 is better.

Kinetical Considerations

In the continuous process, if the decreasing rate of formaldehyde is the first order as to the formaldehyde concentration in the solution, the following relation is to be derived,

$$\frac{1}{S \cdot V} = \frac{1}{k} \ln \frac{a}{a-x},$$

where $a$ is the initial concentration of formaldehyde, $x$ the amount of the formaldehyde decreased at 1/S. V. and $k$ the rate constant. The relations between 1/S. V. and log $(a-x)$ are graphically shown in Fig. 3 from the experimental results. As shown in the

* cf. Fig. 10 in This Journal, 22, 28 (1952).
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figure, the linear relations are established, and so it is confirmed that the decreasing rate of formaldehyde is the first order.

The values of $T_r$ in Table 1 are those of $1/S.V.$ at the intersecting points between the broken line in Fig. 3 which shows the position where the formaldehyde concentration $(a - x)$ is 0.3 g/100 cc and the straight lines drawn by the above equation. As shown in the case of Exp. No. P 3 this linear relation being established even below 0.3 g/100 cc of the formaldehyde concentration, it is permitted to determine the intersecting points by the extrapolation.

As the apparent activation energy related to the rate constant $k$, 20 kcal (calculated from Exp. Nos. P 9 and P 10) is obtained, and this large value compared with the previous work is assured by the fact that the stirring effect on the value of rate constant is not observed.

It seems that the decreasing rate of formaldehyde depends on the pressure of acetylene gas in the experimental results is caused by the unsaturated state of the catalyst surface, and also the fact that the stirring effect is not found in contrast with the previous report results from the slight change of medium due to the reaction products. It is thought from these results that the rate constant in the above rate equation has the connection with the process of the surface reaction.

Conclusions

Among tetrahydrofuran, acetone and methanol, tetrahydrofuran is most excellent as a solvent in the propargyl alcohol synthesis, and it seems to be preferable to use about twofold volume at least to an aqueous formaldehyde solution.

In the experimental results of the continuous process shown in Table 1, the percentage of ratio in moles of the propargyl alcohol formed to the formaldehyde consumed $(P/F)_c$ does not exceed 30% in any case, and even in the case where the space time yield of propargyl alcohol (S.T.Y.) is largest (Exp. No. P 3), its value is only 30.7 g/hr. From these results it seems to be difficult to obtain a large quantity of propargyl alcohol as the main product in a continuous process.

In the experimental results in the static method, $(P/F)_s$ amounts to about 50%. The reason that the yield is better in this case than that in the continuous process depends on the facts that the pressure of acetylene gas is higher and the reaction
temperature is lower.

From these results, in order to gain propargyl alcohol as the main product in performing the continuous reaction procedure using this catalyst in such a manner that the residual formaldehyde does not remain, it seems necessary to take such reaction conditions that more than twofold volume of tetrahydrofuran to an aqueous formaldehyde solution is used, the reaction temperature is below 100°C, pH is kept as low as possible within the range in which the catalyst is not damaged, and the highest possible pressure in the operating procedure is taken. Namely, there lies the difficulty in the point that the large value of (P/F)r is to be expected in the sacrifice of (S. T. Y.); in respect of the reaction temperature and pH. However, it should be noticed that the elevation of pressure of acetylene gas brings about the distinguished positive effect on (P/F)r and (S. T. Y.);

The author has great pleasure in expressing his sincere thanks to Prof. R. Kiyama and Dr. J. Osugi for their valuable guidances during the course of this research.

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