

HYDROGENATION OF THE 2-BUTYN-1,4 DIOL IN SUPERCRITICAL CARBON DIOXIDE

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ABSTRACT

Hydrogenation of 2-butyne-1,4-diol was carried out in a stainless steel reactor under supercritical conditions by using carbon dioxide as solvent. The chromatograms of the reactive mixture showed the presence of several peaks. Written and experimental research has permitted the identification of the corresponding products. The two major products 2-butene-1,4-diol and butane-1,4-diol were formed, along with other by-products like 2-ethoxytetrahydrofuran, which is the result of a reaction between 2-hydroxytetrahydrofuran and ethanol.

INTRODUCTION

Hydrogenation of 2-butyne-1,4-diol produces an intermediate, namely 2-butene-1,4-diol. This olefinic diol has many applications in paper and textile industries. Moreover, it is used in the manufacture of endosulfan, vitamins A and B6 and in the manufacture of resin. Further hydrogenation of 2-butene-1,4-diol yields a saturated product called butane-1,4-diol, which is a useful intermediate in the manufacture of fine chemical products like tetrahydrofuran. A lot of studies have been done on these reactions of hydrogenation by using catalysts (generally made of palladium or platinum) on different supports¹⁻⁵. Zhao et al.^{6,7} have successfully conducted these reactions without using an organic solvent and without adding catalysts, since the wall of the stainless steel reactor promoted the reactions. Thus, these studies show another interesting application of supercritical carbon dioxide in the development of green chemical industrial processes.

The objective of this study is to identify the products of the hydrogenation of 2-butyne-1,4-diol that were produced under our experimental conditions.

MATERIALS AND METHODS

The hydrogenation of 2-butyne-1,4-diol was carried out in a stainless-steel reactor in which it is possible to implement reaction up to 30MPa and 473K. This reactor has a variable speed stirrer, three feeders and one outlet line equipped with a gas-liquid separator (the cyclonic type: in order to limit the drive of the liquid phase). The constant temperature was maintained by the circulation of oil in an external jacket. Safety arrangements like rupture disc and high temperature cut-off were also provided. A photograph of the pilot is given on Figure 1.

In these experiments the pilot is used in batch mode. First, the reactant is introduced into the reactor. Then, liquid carbon dioxide is pumped into the reactor up to 160 bar. The stirrer is set at 400 rpm and a mass flow controller measures the quantity of hydrogen until the total pressure becomes 200

bar. Palladium, which is used as a catalyst, is put into an annular catalyst bed that is fixed on to the impeller.

Hydrogen is highly soluble in carbon dioxide. So, if the mixture is not agitated during the introduction of hydrogen, a pressure drop in the reactor should be observed. This is only due to the slow mixing of hydrogen with carbon dioxide.



Figure 1: photograph of the pilot

The samples were analysed by gas chromatography for reactants and products. The analysis was carried out using a gas chromatograph equipped with a 30 m X 0.32 mm internal diameter TR-wax column, which was fitted with a FID detector. The carrier gas was helium. The column temperature was in the range of 100 to 250°C;

All chemical products were purchased from Sigma-Aldrich or Merck. They had all reached at least 99% of purity.

RESULTS AND DISCUSSION

A bibliographical survey¹⁻⁷ showed that several products could be formed in the course of the reaction. Figure 2 shows a reaction pathway, which was adapted from research on the hydrogenation of 2-butyne-1,4-diol to various products.

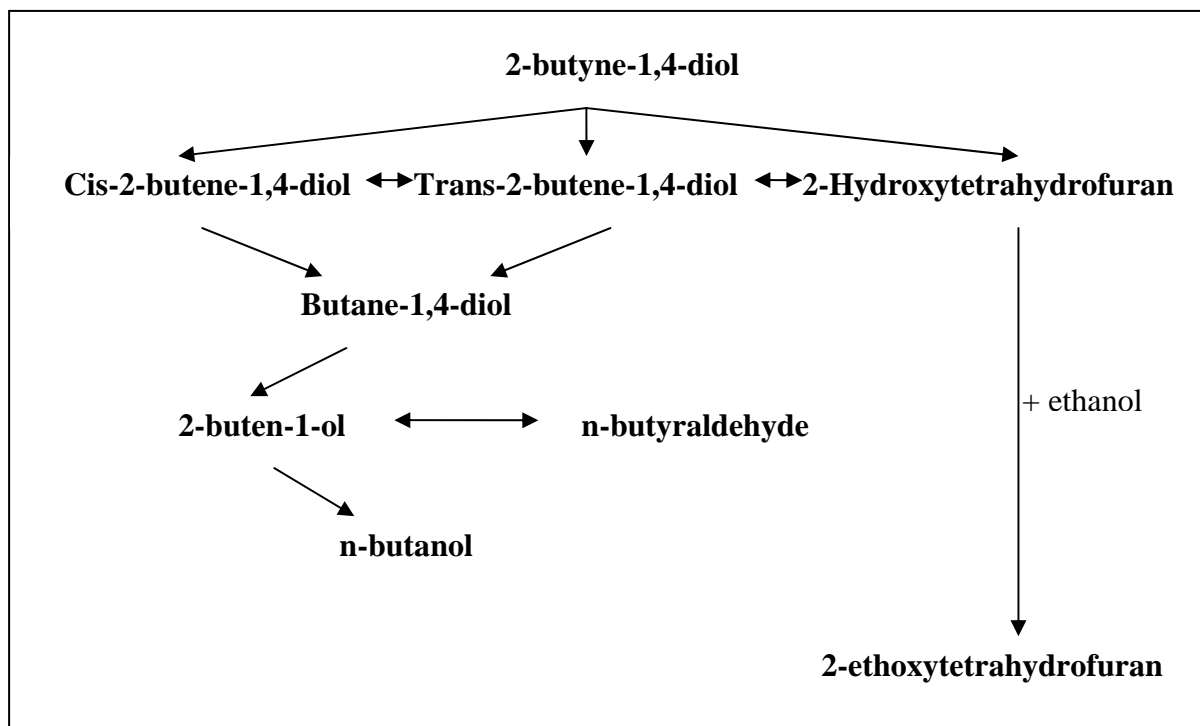


Figure 2: Reactive scheme (→reaction, ↔isomerisation)

Initially, the sequence of temperature programmed was an isothermal run at 210°C. Several peaks were observed on the chromatograms, but some of them were not sufficiently separated from the peaks of ethanol, which is the solvent used to dilute the sample. So, a new program of temperature was used:

- initial oven temperature: 100°C for 1 minute;
- temperature ramp: 15 °C/min up to 210°C;
- final temperature: 210°C for 3 minutes.

It resulted in a better resolution of the peaks.

The non-gaseous components involved in the reaction were identified by two methods.

1. Calibration solutions of the desired products in ethanol were analysed. The corresponding retention time was determined.
2. A sample was analysed a first time. Then a small quantity of the desired product was added into the sample and it is analysed again.

The application of both methods to 2-butyne-1,4-diol, 2-butene-1,4-diol, butane-1,4-diol ensured the quality of the results. For the other components, the use of the second method allowed their rapid detection in the reaction mixture.

In Table 1, the retention time of the three major products is given by using the first method.

Table 1: Retention time of the major compound

<i>Compound</i>	<i>Retention time (second)</i>
2-butyne-1,4-diol	370
Cis-2-butene-1,4-diol	418
butane-1,4-diol	570

On Figure 3, the chromatogram of a sample of the reactive mixture is given. According to the reaction time, the peaks corresponding to the three major products could be easily identified. Nevertheless, a zoom is necessary for the butenediol (Figure 4). Indeed, the sample analyses showed two peaks which could be attributed to the two different forms of the alkene. The addition of cis-butenediol (green curve on Figure 4) showed that only the height of the second peak increased. This proves that both forms are present in the reactive mixture, but the cis-form is mainly produced.

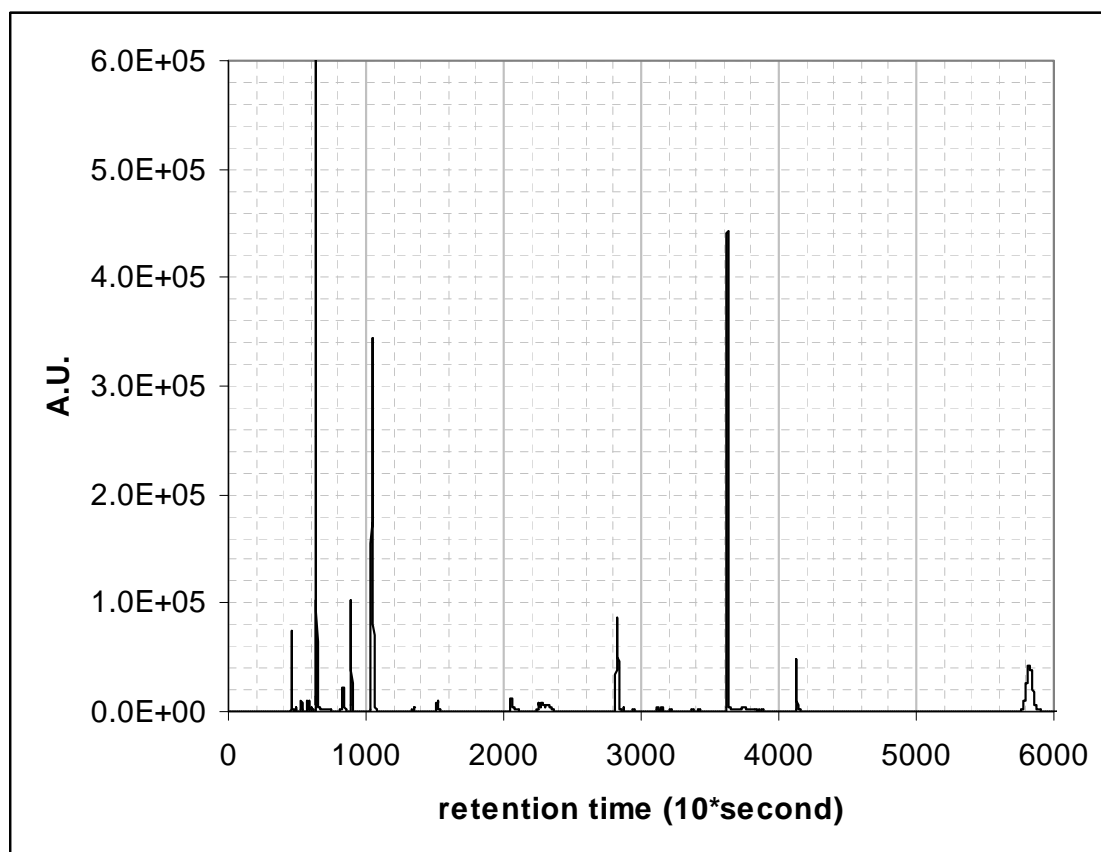


Figure 3: Chromatogram of the reactive mixture

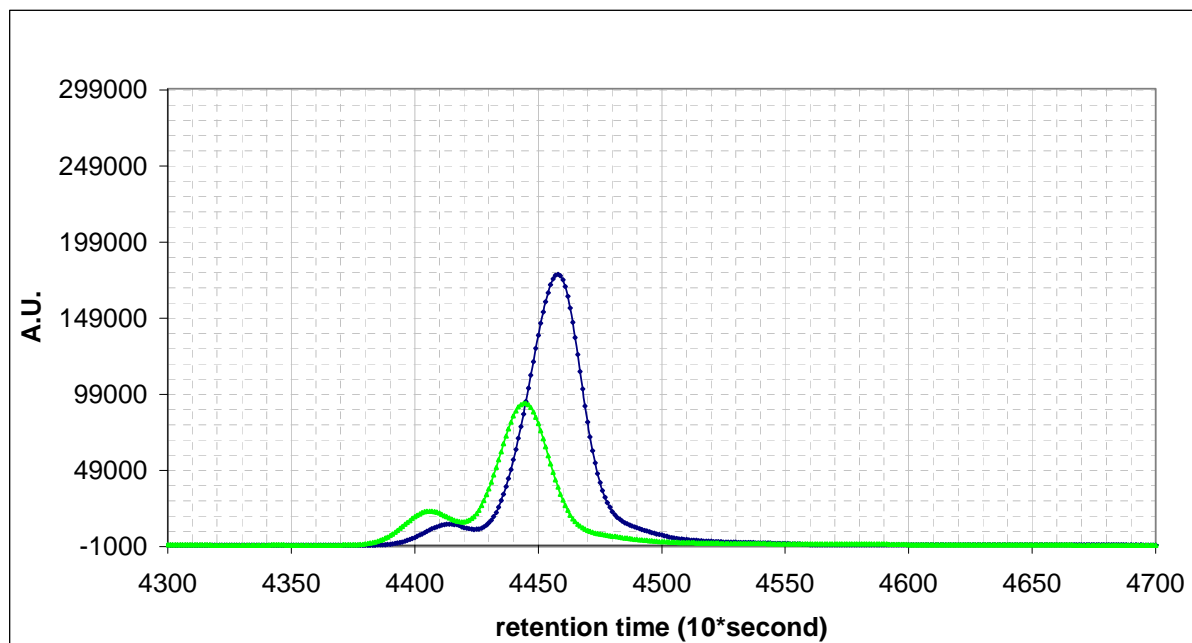


Figure 4: Zoom on the retention time of 2-butene-1,4-diol

The addition of crotylalcohol implied the apparition of a new peak. So, we deduced that it was not present in the mixture sample. The conclusion is the same for n-butyraldehyde and butanol.

The 2-hydroxytetrahydrofuran was not tested because it was not possible to buy it. Nevertheless, we added 2-ethoxytetrahydrofuran to the sample. This product seemed interesting because it could be obtained by the reaction between 2-hydroxytetrahydrofuran and ethanol. Three peaks attested the presence of 2-ethoxytetrahydrofuran (retention times between 78 and 100 seconds). It goes to prove that 2-hydroxytetrahydrofuran is formed during the reaction. However, it should be related to one (or more) of the unidentified peaks on the chromatograms.

CONCLUSIONS

Hydrogenation of 2-butyne-1,4-diol in a stainless steel reactor produces the desired products (2-butene-1,4-diol and butane-1,4-diol). Several peaks products were identified on the gas chromatograms of the samples. Therefore, the retention times of the main products of the hydrogenation reaction are now known, as well as some of the by-products of the reaction. To rapidly obtain the desired products of the hydrogenation, the experiments were made by using a palladium catalyst. Our future objective is to carry out the same reactions, but under operating conditions close to those used by Zhao et al. [5]. Those experiments will be done on a greater scale in order to verify if it is possible to synthesise the desired products without using a catalyst.

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