

The hydrogenation of 2-butyne-1,4-diol over a carbon-supported palladium catalyst

Iain T. Duncanson, Iain W. Sutherland, Bernard Cullen, S. David Jackson, and David Lennon*

Department of Chemistry, Joseph Black Building, University of Glasgow, Glasgow G12 8QQ, Scotland, UK

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The hydrogenation of 2-butyne-1,4-diol in propan-2-ol over a carbon-supported palladium catalyst has been investigated in a batch reactor. At low conversions complete selectivity to *cis*-but-2-ene-1,4-diol is observed. However, further hydrogenation leads to a wide variety of products, most notably 2-isopropoxy-tetrahydrofuran and butane, neither of which have previously been associated with this reaction system. The former is thought to occur as a result of a surface-mediated process, involving the insertion of dissociatively adsorbed solvent molecules. Butane formation is attributed to the double condensation and hydrogenation of a chemisorbed *cis*-but-2-ene-1,4-diol intermediate. The alkane preferentially partitions in the gaseous phase, which results in an marked mass imbalance for the liquid phase. A reaction scheme is presented to rationalise these observations.

KEY WORDS: 2-butyne-1,4-diol; hydrogenation; Pd/C; *cis*-but-2-ene-1,4-diol; liquid phase hydrogenation.

1. Introduction

Butane-1,4-diol (global production capacity ca. 910 kilotonnes p.a.) is an important chemical feedstock, which is used in the production of tetrahydrofuran, polybutenepthalate and polyurethanes [1]. The manufacturing process typically involves the conversion of ethyne to 2-butyne-1,4-diol, which is then hydrogenated to butane-1,4-diol. Partial hydrogenation to 2-butene-1,4-diol is also beneficial, as this trifunctional molecule can be used to form a precursor of the Thiodan® insecticide [1] and in the production of vitamin B₆[2].

The hydrogenation of 2-butyne-1,4-diol has been studied over a variety of different catalysts including nickel and nickel–copper based systems, which require severe conditions [3,4]. The use of milder conditions is desirable, as it can improve the selectivity towards *cis*-2-butene-1,4-diol. This has been achieved through the use of precious metal catalysts such as palladium. Winterbottom *et al.* [3] have established a general reaction scheme for the reaction, using a 5% Pd/C catalyst. Their scheme consists of two stages: (i) adsorption and reduction of 2-butyne-1,4-diol to form *cis*-2-butene-1,4-diol via a consecutive mechanism; and (ii) further reduction of *cis*-2-butene-1,4-diol to form butane-1,4-diol, along with a variety of side products. The side products observed were *cis*- and *trans*-crotyl alcohol and *n*-butanal, the latter formed via isomerisation of a crotyl alcohol intermediate [3]. Telkar *et al.* [5], investigating the hydrogenation of 2-butyne-1,4-diol over a range of supported palladium catalysts, proposed a second scheme

whereby *n*-butanal was formed via γ -hydroxybutanal, itself formed via isomerisation of *cis*-2-butene-1,4-diol. Subsequent work by Musolino *et al.* additionally reported the formation of 2-hydroxytetrahydrofuran during the hydrogenation of 2-butyne-1,4-diol over a 0.5% Pd/C catalyst [6], with this compound formed via an intramolecular reaction of γ -hydroxybutanal to form the cyclic hemiacetal 2-hydroxytetrahydrofuran [6]. Musolino *et al.* also report the formation of 2-ethoxytetrahydrofuran [6], and propose that it is formed via the reaction of the solvent (ethanol) with 2-hydroxytetrahydrofuran. The acidic nature of the carbon support is thought to promote the formation of both 2-hydroxytetrahydrofuran and 2-ethoxytetrahydrofuran [6].

This communication addresses the hydrogenation of 2-butyne-1,4-diol in the liquid phase using a carbon-supported palladium catalyst that yields a broad range of products. Firstly, it identifies the formation of 2-isopropoxy-tetrahydrofuran and butane as products not previously associated with this reaction. Then, quantification of the 2-isopropoxy-tetrahydrofuran reveals a substantial mass imbalance for the solution phase, which is primarily attributed to butane production. Finally, a reaction scheme is proposed that identifies the range of chemical pathways accessible within this industrially relevant reaction system.

2. Experimental

A 1% palladium/carbon supported catalyst was used in this study. It was prepared from palladium(II) nitrate (Alfa Aesar, 99%) and Norit RX3 carbon using the incipient wetness technique. The preparation and

*To whom correspondence should be addressed.

E-mail: d.lennon@chem.gla.ac.uk

characterisation of the catalyst (6.2×10^{18} Pd_(s) g⁻¹, 11% dispersion, surface area 1118 m² g⁻¹, mean palladium particle size ca. 10 nm) have been described elsewhere [7,8]. The catalyst was ground and sieved to a particle size of 250–500 μm prior to reaction testing. Reactions were performed in a Büchi stirred autoclave at a hydrogen pressure of 3 atm, and with propan-2-ol (BDH, 99.7%) as the reaction solvent. The autoclave was fitted with an on-demand gas delivery system (Büchi Pressflow). About 100% conversion is defined as the consumption of 1 mole equivalent of dihydrogen, relative to 2-butyne-1,4-diol. Analysis was performed using an off-line gas-liquid chromatograph (Perkin-Elmer 8500) equipped with an FID and fitted with a capillary column (SGE BP20, length 30 m, 0.25 mm ID, 0.32 mm OD). Additional analysis was carried out by ¹H NMR spectroscopy (Bruker DPX, 400 MHz) and by GC-MS (HP 6890 with JEOL JMS-700).

Approximately 1.00 g of the catalyst was activated *in situ* by passing hydrogen (BOC, 99% purity) at 0.3 l min⁻¹ through a slurry of the catalyst in propan-2-ol (BDH, ≥ 99.7% purity) at 338 K for 30 min with agitation (300 rpm). A de-gassed solution of ca. 8.00 g of 2-butyne-1,4-diol (Aldrich, 99%) in propan-2-ol was then introduced to the reaction vessel. A constant hydrogen pressure of 3 atm was maintained throughout the reaction, and the reaction mixture was agitated at 800 rpm. The reaction sequence presented was replicated on numerous occasions. All reactions were carried out at a temperature of 338 K.

3. Results and discussion

This reaction profile for the hydrogenation of 2-butyne-1,4-diol in isopropyl alcohol over the Pd/C catalyst at 338 K is shown in figure 1. The initial product was, as expected, *cis*-2-butene-1,4-diol. The observed high selectivity (100% at $t=75$ min, 43% conversion;

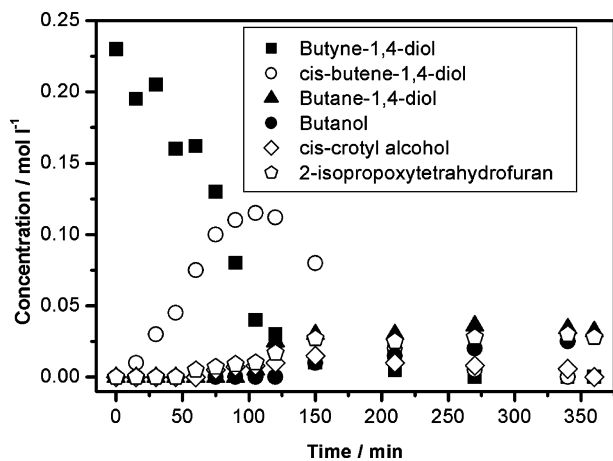


Figure 1. Reaction profile for the hydrogenation of 2-butyne-1,4-diol in propan-2-ol over 1% Pd/C.

73% at $t = 100$ min, 65% conversion) is in accordance with the results reported previously in the literature [3,5,6]. Over the first 100 min the reaction rate corresponds to 4.2×10^{20} 2-butyne-1,4-diol molecules min⁻¹, which translates to a turnover frequency of 68 molecules min⁻¹ Pd_(s)⁻¹. Following around 82% conversion of the starting material (approximately 105 min), the alkene-diol was further reduced to form the alkanediol (butane-1,4-diol).

In addition to butane-1,4-diol, *cis*-2-butene-1,4-diol formed a variety of side products in a concurrent manner. The majority of these side products were identified by a combination of GLC and ¹H NMR spectroscopy, and included butan-1-ol, 3-butene-1-ol, and *cis*- and *trans*-crotyl alcohol. These results are in broad agreement with those previously reported in the literature [3,5,6]. However, importantly, it is noted that no *n*-butanal, γ -hydroxybutanal, nor 2-hydroxytetrahydrofuran was observed during the course of this reaction. Additionally, an initially unknown product was produced, and in comparable quantities to those of butane-1,4-diol, the expected major product at this stage of the reaction [3,5]. GC-MS studies showed this species to have a molecular weight of 130 amu. ¹H NMR spectroscopy showed a distinctive doublet at 5.22 ppm and, crucially, no peaks downfield of 5.75 ppm, showing conclusively that neither γ -hydroxybutanal nor *n*-butanal were present, as the presence of an aldehyde would result in peak at approximately 10 ppm [9]. On the basis of GC-MS and ¹H NMR data [10], the unknown species observed was identified as 2-isopropoxy-tetrahydrofuran [(C₄H₃O)-OCH(CH₃)₂]. This product has not previously been associated with the catalytic hydrogenation of 2-butyne-1,4-diol.

All products were quantified via the use of standards (Aldrich) to obtain an FID response factor, with the exception of 2-isopropoxy-tetrahydrofuran, for which no standard was commercially available. This species was quantified by comparison of the integrals of its unique ¹H NMR signal at 5.75 ppm [10] with a signal from an internal standard (*cis*-crotyl alcohol). From this, the concentration of the 2-isopropoxy-tetrahydrofuran in any sample could be determined. Correlation of the concentration determined by ¹H NMR spectroscopy with the GLC peak area over a broad concentration range allowed the construction of a calibration curve for this unexpected product. The resulting GLC response factor for 2-isopropoxy-tetrahydrofuran is significantly higher than its C₄ counterparts and has direct repercussions in determining the mass balance for this reaction system.

A carbon mass balance for the above reaction profile (figure 1) is presented in figure 2. The mass balance shows a dramatic drop at ca. 120 min (ca. 85% conversion of 2-butyne-1,4-diol), which corresponds to the maximum accumulation of *cis*-butene-1,4-diol. At this point the mass balance drops from ca. 100% to ca. 45%,

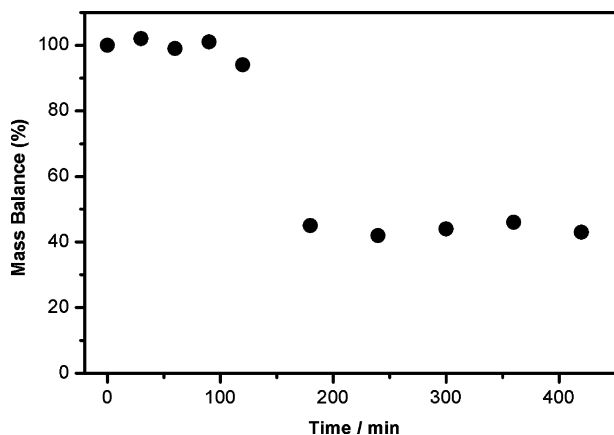


Figure 2. Carbon mass balance for the hydrogenation of 2-butyne-1,4-diol in propan-2-ol over 1% Pd/C.

where it remains effectively constant thereafter. Throughout this transition period, the hydrogen consumption remains constant, indicating no discontinuity in the overall hydrogenation process. Somewhat surprisingly, GLC and GC-MS analysis of the reaction medium detected the presence of butane at this stage. Due to the low solubility of butane in the reaction solvent (x_{butane} in propan-2-ol = 0.1179 at $p = 1.013$ bar [11]), the majority of this product will exist in the gas phase. This partitioning of the butane from the gas phase to the liquid phase is believed to be primarily responsible for the mass imbalance presented in figure 2, which corresponds to the liquid phase only.

Comparison between figures 1 and 2 shows that the onset of production of the C₄ products, derived from

cis-butene-1,4-diol, corresponds to the discontinuity in the mass-balance. The available reaction pathways observed for this reaction system are shown in figure 3.

It is acknowledged that the formation of 2-isopropoxy-tetrahydrofuran could be the result of an acetal formation reaction between the solvent and 2-hydroxy-tetrahydrofuran, promoted by an acidic support material. Indeed, carbonaceous supports similar to that used in this study have been shown to exhibit amphoteric properties [12]. However, no 2-hydroxy-tetrahydrofuran, nor its precursor γ -hydroxybutanal, was detected at any time during the course of this work. Experiments with the carbon support material alone have established that no conversion of 2-butyne-1,4-diol occurs in the absence of palladium. It is recognised that this “blank” experiment only indicates that the initial process is metal-mediated, and that the alternative stoichiometric route to formation of the acetal (2-isopropoxy-tetrahydrofuran) requires hydrogenation and isomerisation centers (Pd?) to form the γ -hydroxybutanal intermediate from the alkynediol. Nevertheless, apart from the absence of any of the possible reaction intermediates for this stoichiometric chemistry, it is also doubted that the carbon support can be acting as such a prominent proton donor. Furthermore, acetal formation mechanisms proceed with elimination of water [13]. In a closed system such as that used in this study (i.e. where water is not removed from the system) this water will remain within the system and could result in hydrolysis of the acetal back to the hemiacetal [13], although it is recognised that both the relatively high dilutions used, and the presence of the carbon support

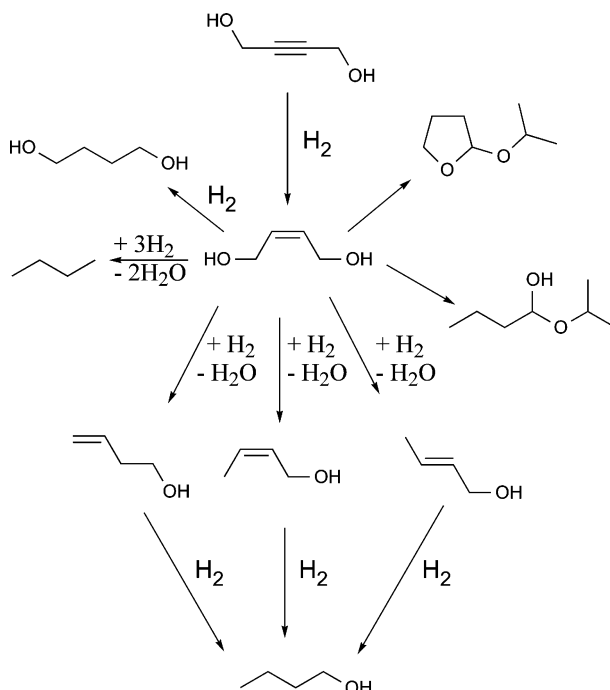


Figure 3. Reaction scheme showing all observed products of the hydrogenation of 2-butyne-1,4-diol in propan-2-ol over 1% Pd/C.

could partially mitigate this effect. However, nevertheless, it is doubted that this could result in the absence of any observable hemiacetal.

In an additional exploration of probable routes to the formation of the 2-isopropoxy-tetrahydrofuran, experiments in which the Pd/C catalyst was filtered from the reaction mixture mid-reaction showed no further reactivity once the catalyst has been removed, thus showing that a homogeneous Pd complex is not responsible for the observed chemistry. Traditional catalytic routes to substituted furans typically rely on homogeneous complexes and oxidising conditions [10] or stoichiometric methods [14].

Collectively, these observations indicate that, for the system under investigation here, the origins of 2-isopropoxy-tetrahydrofuran do not appear to be directly associated with conventional stoichiometric organic reactions or homogeneous Pd complexes post-first stage hydrogenation (i.e. originating from *cis*-2-butene-1,4-diol). Given that the alkynediol \rightarrow alkanediol conversion is thought to be a surface process [3] and that the hydrogenation of butenes over transition metal surfaces can lead to a variety of reaction products [15], it is suggested that the formation of the 2-isopropoxy-tetrahydrofuran could also be a surface mediated process. Tentatively, it is proposed that this product forms via the insertion of an isopropoxy group (formed by the dissociative adsorption of a propan-2-ol molecule onto the catalyst surface [16]) at the 1-position of an adsorbed C₄ molecule, followed by cyclisation to yield 2-isopropoxy-tetrahydrofuran. Work is currently underway in our laboratories to explore this prospect further.

It is noted that a small quantity ($<0.005 \text{ mol l}^{-1}$) of 1-isopropoxy-butan-1-ol is also detected in the reaction medium. The formation of this entity is believed to be linked with the production of 2-isopropoxy-tetrahydrofuran, with the exclusion of the ring closure process. The dominance of 2-isopropoxy-tetrahydrofuran over the linear analogue indicates ring closure to be the favoured process.

Unfortunately, it is not possible to readily quantify the extent of butane formation, due to the alkane's tendency to partition in the gas phase [11]. The reduction of alcohols to alkanes is unfavourable under these conditions [17] and, consequently, the butane formation is not attributed to the hydrogenation of butan-1-ol in figure 3. Rather, the butane formation is thought to occur as a consequence of the symmetry of the 2-butene-1,4-diol molecule. Loss of a single alcohol unit under reducing conditions to form 2-butene-1-ol is an established process [3], therefore, it is believed to be not unreasonable that a simultaneous condensation/hydrogenation reaction could occur at the C₁ and C₄ positions to yield the alkane. It is also noted that dehydroxylation at this stage of the reaction sequence could lead to retained hydrocarbonaceous species [18], which could contribute to catalyst deactivation. Retention of hydrocarbon reagents

in this manner would also contribute to the carbon imbalance shown in figure 2. However, given that the hydrogen up-take about the transition to a negative mass balance remained continuous, it is anticipated that the extent of any carbon retention about this juncture is small and cannot account for the loss of 55% of mass from the liquid phase reagents. Carbon retention to such a degree corresponds to ca. 4900 C₄ molecules for every Pd surface atom, which would immediately deactivate the catalyst and, as figure 1 illustrates, *cis*-but-2-ene-1,4-diol continues to be progressively hydrogenated up to full conversion (200% conversion with respect to 2-butyne-1,4-diol) beyond this time. Thus, any carbon deposition at this stage is thought to be minimal and is seen not to detrimentally affect activity. Consequently, the majority of the mass imbalance is therefore attributed to butane formation via the double condensation and hydrogenation of a chemisorbed *cis*-but-2-ene-1,4-diol intermediate. To the best knowledge of the authors, the possibility of this additional pathway has not previously been appreciated, and an awareness of its probable occurrence is important in understanding the variety of options possible in the liquid phase hydrogenation of 2-butyne-1,4-diol over supported palladium catalysts.

Moreover, this investigation indicates an alternative preparative route to substituted furans and molecules with direct links to carbohydrate chemistry. Interestingly, the process has been shown to be generic, with the alkoxy group inserted in this system varying according to the alcoholic solvent used, thus providing a broader range of synthetic possibilities. A full mechanism has been developed and will be presented elsewhere [19].

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