

Hydrogenation of Benzonitrile over Supported Pd Catalysts: Kinetic and Mechanistic Insight

Mairi I. McAllister,[†] Cédric Boulho,[†] Lauren F. Gilpin,[†] Liam McMillan,[†] Colin Brennan,[‡] and David Lennon^{*,†}

[†]School of Chemistry, Joseph Black Building, University of Glasgow, Glasgow G12 8QQ, U.K.

[‡]Syngenta, Jeallot's Hill International Research Centre, Berkshire RG42 6EY, U.K.

ABSTRACT: The liquid phase hydrogenation of benzonitrile over a 5 wt % Pd/C catalyst using a stirred autoclave is investigated. The reaction conforms to a consecutive reaction sequence: first benzonitrile is hydrogenated to produce benzylamine, which subsequently undergoes a hydrogenolysis step to form toluene. Benzonitrile hydrogenation obeys first-order kinetics with an activation energy of 27.6 kJ mol⁻¹. In contrast, the benzylamine hydrogenolysis stage obeys zero-order kinetics and exhibits an activation energy of 80.1 kJ mol⁻¹. A 1 wt % Pd/Al₂O₃ catalyst is additionally examined, which is also seen to support hydrogenolysis activity alongside the hydrogenation pathway. Gas phase transmission infrared spectroscopic measurements of the hydrogenation of benzonitrile and benzylamine over the 1 wt % Pd/Al₂O₃ catalyst utilizing hydrogen and deuterium are undertaken, which enable reaction schemes incorporating adsorption geometries of intermediate adsorption complexes to be proposed.

KEYWORDS: nitrile hydrogenation, carbon-supported palladium, hydrogenolysis, benzonitrile, benzylamine

1. INTRODUCTION

Primary aromatic amines represent an important class of chemicals with widespread application in many areas of the chemical industry.¹ Several different routes to these compounds are available, including the heterogeneously catalyzed hydrogenation of nitriles.² A particular example of this would be the industrial production of hexamethylenediamine, a precursor of nylon-6,6, via the heterogeneously catalyzed hydrogenation of adiponitrile.³ Typically, skeletal metal catalysts, such as Raney Co or Raney Ni,^{4,5} have been favored for hydrogenations of fine chemicals due to a high resultant selectivity. Nevertheless, such catalysts are often found to be too active in a fine chemicals environment, where additional functionality may be compromised by overhydrogenation.⁶ As a result, use of supported Pd catalysts has become a more favorable choice to facilitate the transformation of the nitrile functionality.

The hydrogenation of a range of aromatic nitriles over a commercially available 5 wt % carbon supported Pd catalyst has recently been reported by McMillan and co-workers.^{7,8} One of the substrates considered, benzonitrile, was notable due to the occurrence of a hydrogenolytic pathway alongside hydrogenation of the nitrile moiety that resulted in the selective production of toluene. As the simplest aromatic nitrile, benzonitrile provides a good bridging point between aliphatic nitriles, already extensively researched,^{9–11} and more complex, substituted species that have greater industrial relevance in several sectors of the chemical manufacturing industry such as agri-chemicals, pharmaceuticals, and fine chemicals. A number of other researchers have also reported on this topic, and related reaction systems, as outlined below.

On examining the liquid phase hydrogenation of benzonitrile over a Pd/C catalyst, in 2005 Hegedüs and Máthé reported complete nitrile conversion and high benzylamine

selectivity (95%).¹² The high selectivity toward the primary amine was obtained under mild conditions (303 K, 6 bar H₂) in the presence of an acid additive. Nonetheless, the presence of a hydrogenolysis pathway to yield toluene was also acknowledged.¹² Similarly, the presence of a hydrogenolysis step as a side reaction when hydrogenating nitriles was also reported by Yap and co-workers.^{13,14}

Historically, this heteroatom cleavage has not been a predominant feature of the heterogeneous catalysis literature, with the phenomenon thought to be the dominant process of the reaction only under “harsh” reaction conditions.^{14,15} Despite this, selective production of the hydrogenolysis product under mild conditions has been reported; for example, by Maschmeyer et al.,¹⁴ through the study of benzonitrile over a Pd/C catalyst. Given the industrial importance of primary amines, the occurrence of concurrent or consecutive hydrogenolysis pathways alongside hydrogenation reactions constitutes a topic worthy of further investigation.

Interestingly, the hydrogenation of 4-hydroxybenzyl cyanide to form tyramine studied by McAllister and co-workers did not yield the hydrogenolysis product (4-hydroxyethylbenzene).⁸ This outcome was rationalized with reference to work undertaken by Maschmeyer et al.,¹³ which proposed that it is the positioning of the aromatic group with respect to the heteroatom that dictates the viability of a posthydrogenation hydrogenolysis stage for aromatic nitriles. If the α -carbon, with respect to the heteroatom, is adjacent to the aromatic ring then stabilization of the carbon by the aromatic ring may occur making cleavage under mild conditions favorable. Thus, as is the case for tyramine, when the α -carbon is not adjacent to the

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aromatic ring, the phenomenon cannot occur and hence heteroatom cleavage is not observed.⁸

Examining the hydrogenolysis process further, Maschmeyer and co-workers found that on substrates with aromatic groups adjacent to the nitrile functionality, a greater degree of hydrogenolysis could be achieved by using a high catalyst loading. Subsequent kinetic investigation by this group identified that the hydrogenation of benzonitrile was first-order but, conversely, the hydrogenolysis of benzylamine was found to be zero-order. Zero-order kinetics are often observed when the catalyst active sites are fully saturated with the substrate due to favorable substrate–surface interactions. This finding was hence attributed to strong benzylamine adsorption to the catalyst surface.¹⁴

Bakker et al. further highlight the importance of this hydrogenolytic pathway in their study of the hydrogenation of benzonitrile over a 5 wt % alumina supported Pd catalyst, where toluene ($C_6H_5CH_3$) was observed as a byproduct.¹⁶ A role for a Pd–H phase at the catalyst surface that is populated at hydrogen pressures in excess of 10 bar was thought to be responsible for preventing the hydrogenolysis reaction, while increasing the formation of the coupling product dibenzylamine.¹⁶ It is suggested that the toluene can be formed by two distinct processes: (i) hydrogenolysis of benzylamine and (ii) direct hydrogenolysis of benzonitrile.¹⁶

The liquid phase, variant of this reaction is predominant in the literature with a number of factors identified as important in achieving high selectivity; these include catalyst choice, reaction conditions, the starting material, and hydrogen availability.^{17,18} In a move toward the selective production of benzylamine, more exotic experimental conditions have been examined. For example, Chatterjee et al. report, in the absence of additives, both high conversion (90%) and selectivity (91%) in supercritical CO_2 over a Pd/MCM-41 catalyst.¹⁹ While this methodology shows promise for “clean” chemical processes, the energy demands associated with supercritical CO_2 , at present, lowers the overall efficiency of the process.

As an extension, however, continuous hydrogenation of benzonitrile in the gas phase is comparatively less well studied.^{20–22} Such studies note that residence time also plays a key role in achieving high selectivity to the desired product.²⁰ Moreover, a shorter contact time in a continuous gas phase operation can prevent condensation of the imine with benzylamine to yield unwanted byproducts.^{20,22} Keane and co-workers report that, while toluene was the predominant product of benzonitrile hydrogenation over Pd/C, it was benzylamine that was favored over Pd/ Al_2O_3 . Despite this, hydrogenolysis to toluene was observed at the higher contact times required for sufficient conversion to be achieved. The use of multiple Pd/ Al_2O_3 beds in series was thus used as a successful means of retaining full benzylamine selectivity.²²

Use of a Pd/ Al_2O_3 catalyst in the hydrogenation of benzonitrile in a fixed-bed reactor has also been employed by Zhang et al.²³ Deactivation studies on this system indicated that the loss in activity observed at extended run times could be attributed to carbonaceous compounds deposited on the surface of the catalyst. The irreversibility of the bonding of these species to the surface causes loss of catalytic activity as a consequence of active site obstruction.

With reference to the aforementioned literature, it is clear that there are complications, particularly under liquid phase batch conditions, arising in the hydrogenation of benzonitrile. The batch variant of this process is commonly plagued by

unwanted side reactions such as hydrogenolysis to yield toluene,⁷ compromising primary amine yield. Further insight into the interconnectivity of the hydrogenation and hydrogenolysis pathways associated with benzonitrile hydrogenation over heterogeneous Pd catalysts in the liquid phase is therefore desirable.

Against this background, further investigation into the hydrogenation of benzonitrile over the same 5 wt % Pd/C reference catalyst used in previous investigations of aromatic nitrile hydrogenations by McMillan and McAllister^{7,8} is reported here. The results section of the paper comprises four parts. Section 1 examines the kinetics and energetics of the liquid phase process over the 5 wt % Pd/C reference catalyst in order to ensure this catalyst's connectivity to recent literature studies. With those benchmark measurements undertaken and the applicability of the autoclave measurements established, section 2 undertakes a new analysis of the kinetic data in order to establish the conformity of the hydrogenation/hydrogenolysis stages to a consecutive process. Following this, section 3 briefly examines the effectiveness of (i) Adams catalyst (PtO_2) and (ii) a 1 wt % Pd/ Al_2O_3 catalyst for benzonitrile hydrogenation in the liquid phase. Finally, section 4 addresses mechanistic issues utilizing the 1 wt % Pd/ Al_2O_3 catalyst applied to the gas phase hydrogenation of benzonitrile and benzylamine, with an adapted IR gas cell acting as a batch reactor that can be operated with either hydrogen or deuterium as the reductant. Identification of deuterium incorporation within the benzylamine and toluene products provides new information on the form of the adsorption complexes linked to the hydrogenation and hydrogenolysis steps. Consequently, reaction schemes are proposed to describe (i) the deuteration of benzonitrile resulting in the formation of toluene- d_3 and (ii) the direct deuterolysis of benzylamine resulting in formation of toluene- d_1 .

2. EXPERIMENTAL SECTION

2.1. Liquid Phase Reactions. The liquid phase hydrogenation reactions were carried out in a 500 mL stirred autoclave (Büchi Glas Uster). An automated gas flow controller (BPC 1202) allowed the delivery of inert (N_2 , BOC, 99.999% purity) and active (H_2 , BOC, $\geq 99.995\%$ purity) gases directly to the reactor via a gas reservoir. The reaction vessel was heated by silicon oil passed around the double jacketed reactor via a heating circulator (Julabo F25). The hydrogen uptake provided a direct indication of reaction rate and hydrogen consumption.

The reactor was first charged with the catalyst (500 mg), and solvent (300 mL propan-2-ol; Riedel-de Haën, 99.5% purity) prior to being purged with inert gas (N_2). Reduction of the catalyst under 4 barg of hydrogen at 300 r.p.m. was carried out for 1 h while the catalyst/solvent mixture was heated to reaction temperature (333 K). In a separate vessel, ca. 17 mmol of the reagent (benzonitrile; Sigma-Aldrich, 99.9% purity or benzylamine; Sigma-Aldrich, 99% purity) was dissolved in 50 mL of solvent and degassed under a constant flow of helium (He , BOC, 99.999% purity). Upon addition of the solubilized and degassed reagent, stirring was stopped, the reactor was sealed, and the hydrogen pressure was raised. Once the reaction pressure (4 barg) was obtained, the reaction mixture was stirred at 800 r.p.m. and samples were taken periodically via an outlet valve throughout the course of the reaction. An agitation rate of 800 r.p.m. corresponded to the

plateau region of a plot of benzonitrile consumption rate versus agitation speed, indicative of operation under a chemical/kinetic regime. No auxiliary reagents, e.g. acid, were used in any of the test reactions. All reactions were performed at least in duplicate, with representative profiles presented here.

Liquid samples were collected periodically and filtered (Minisart 0.2 μm single use sterile filter) to remove any catalyst residue with analysis being undertaken off-line. Gas-liquid chromatography (GLC) analysis was carried out on a PerkinElmer 8500 Series Gas Chromatograph fitted with a Varian Chrompack CP-Sil 8 CB column (30 m \times 0.20 mm ID, 0.33 μm film). Initial concentration of starting material (A_0) values were calculated based on the amount of preweighed starting material added to the reactor prior to commencement of reaction. Errors in GLC output and hydrogen consumption were determined by repeat analysis of a known stock of standards and repeat reactions respectively, with both being found to be below 5%.

For the purposes of this study three catalysts have been used. The primary catalyst utilized for the liquid phase investigation of benzonitrile hydrogenation was a commercial grade 5 wt % Pd/C (Sigma-Aldrich, code number: 205680). This sample was intended to represent a generic hydrogenation catalyst similar to that typically encountered in a fine chemicals setting. The number of Pd surface atoms per gram of catalyst, calculated from CO adsorption isotherms, was found to be 1.11×10^{20} corresponding to a metal dispersion of 39% and a mean particle size of 2.8 nm. The catalyst exhibited a BET surface area of $774 \pm 19 \text{ m}^2 \text{ g}^{-1}$, with the error representing the standard deviation of three replicate measurements. Further characterization of this catalyst is reported elsewhere.⁷

Two other catalysts were examined to a lesser degree. First, due to the Adams catalyst (PtO_2) being reported as a generic hydrogenation catalyst effective in preserving the amine functionality in nitro group reduction reactions,^{24–28} a commercial grade PtO_2 (Sigma-Aldrich, code number: 206032) was briefly investigated. Second, an in-house 1 wt % Pd/ Al_2O_3 catalyst previously used in IR analysis of gas phase catalytic reactions was additionally explored. The 1 wt % Pd/ Al_2O_3 catalyst was prepared via a wet impregnation process that is described elsewhere.^{29,30} Carbon monoxide adsorption isotherm measurements established a value of 7.6×10^{18} surface palladium atoms per gram of catalyst, corresponding to a metal dispersion of 13.4% and a mean particle size of 8.3 nm. The catalyst exhibited a BET surface area of $196 \text{ m}^2 \text{ g}^{-1}$.³⁰

2.2. Vapor Phase Infrared Spectroscopic Measurements. The 1 wt % Pd/ Al_2O_3 catalyst was selected for use in the gas phase IR experiments. The lower Pd loading compared to the reference Pd/C catalyst facilitated a slower benzonitrile conversion, thereby enabling the acquisition of sufficient IR spectra with an acceptable signal-to-noise ratio to define a reaction profile over the full reaction coordinate (i.e., benzonitrile \rightarrow benzylamine \rightarrow toluene). A methodology used previously was adopted.^{30,31} Briefly, the apparatus consisted of a modified heated gas cell (Graseby-Specac 5660) housed within a Nicolet-Avatar 360 FTIR spectrometer.^{30,31} The IR cell was connected to the spectrometer's internal gas purge facility via rubber bellows, thereby ensuring that there were minimal complications to the resultant IR spectra as a result of contributions from atmospheric water or carbon dioxide signals. Brooks mass flow controllers allowed delivery of inert (He, BOC, 99.999% purity) and active (H_2 ,

BOC, $\geq 99.995\%$ purity and D_2 , BOC, $>99.8\%$ purity) gases to be delivered directly to the reactor.

Approximately 500 mg of the 1 wt % Pd/ Al_2O_3 catalyst were placed in a glass boat and loaded into the gas cell outside of the path of the IR beam, ensuring only gaseous species were analyzed during the reaction. The catalyst was reduced under a flow of 10% H_2 /90% He at a rate of 20 mL min^{-1} while being heated to 353 K. The hydrogen composition was subsequently increased to yield an equimolar mixture of hydrogen and helium at a constant flow rate. After 10 min the reactor exit valve was closed allowing a pressure of 1.2 bar to build. At this pressure, the reactor entrance valve was closed, sealing the reactor. A liquid chromatography syringe (Hamilton Bonaduz) was used to inject a 10 μL aliquot of nitrile reagent into the reactor via a septum.

In situ measurements of the gas phase species were recorded as a function of time, with $t = 0$ being defined as the time the injection of the liquid phase reagent into the reactor was complete. Infrared spectra were recorded at a resolution of 4 cm^{-1} by the coaddition of eight scans. This procedure resulted in a total acquisition time of approximately 10 s. The reacting gases obey the Beer-Lambert law, thereby permitting the reliable calibration of reagents by the integration of infrared intensity of particular vibrational features. Due to overlap of diagnostic aromatic and aliphatic CH stretching bands with those of toluene, quantification of benzylamine could not easily be determined. Nevertheless, it was possible for semi-quantitative reaction profiles to be constructed. All measurements were performed at least in duplicate, with representative data sets presented here.

3. RESULTS

3.1. Kinetic Studies (Liquid Phase, 5 wt % Pd/C).

3.1.1. Benzonitrile Hydrogenation: Reaction Order and Energetics. McMillan and co-workers previously reported on benzonitrile hydrogenation over the same 5 wt % Pd/C catalyst under consideration here.⁷ On cessation of hydrogen uptake, indicating reaction completion, the nitrile species was fully converted, but it was the hydrogenolysis product toluene, formed following the hydrogenation step, which was produced with 100% selectivity.⁷ Interestingly, there were no coupling reactions to form the corresponding higher amines in this instance. This finding is attributed to the catalyst choice. Supported Pd is found to be an effective catalyst for both hydrogenation and hydrogenolysis reactions. As a consequence of this, the concentration of both the imine intermediate and benzyl amine will be low in the system due to the occurrence of hydrogenation and hydrogenolysis of these molecules, respectively. This then means that both of the species required for coupling to form the secondary amine (dibenzylamine) are not prevalent in the reaction mixture, thus providing a rationale for the absence of dibenzylamine formation in a system without additives. As an extension of McMillan's studies,⁷ the rate law and energetics of both hydrogenation and hydrogenolysis processes are explored here.

Analysis of the benzonitrile concentration versus time data set at 333 K, where the experimental data are evaluated for correspondence to first-order kinetics, is presented in Figure 1. A highly correlated linear plot is obtained, indicating the reaction conforms to a first-order regime. An associated rate coefficient of $5.9 \times 10^{-2} \text{ min}^{-1}$ is obtained. This outcome is in agreement with Maschmeyer et al., who also reported that

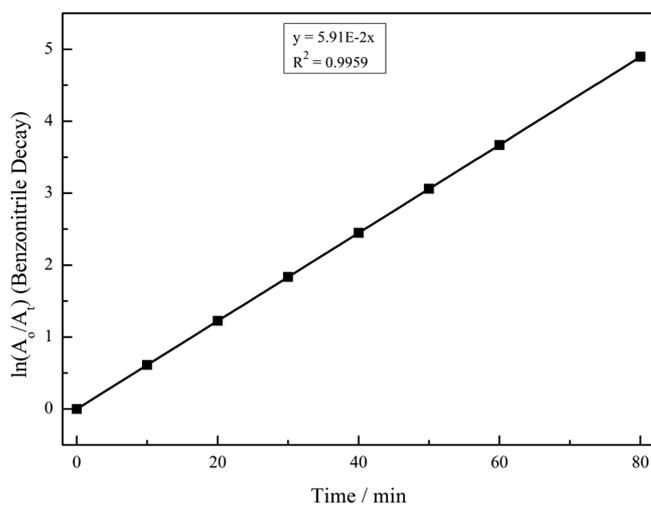


Figure 1. First-order data fit ($\ln(A_0/A_t)$ versus time) for benzonitrile hydrogenation over Pd/C at 333 K, 4 barg, 800 r.p.m. and ca. 17 mmol benzonitrile. A_0 and A_t represent initial concentration and concentration at time t , respectively.

benzonitrile hydrogenation over a Pd catalyst followed first-order reaction kinetics.¹⁴

Reaction temperature, varied within the range 303–333 K, was found to have a significant effect on the initial rate of reaction. A series of first-order plots used for the calculation of rate coefficients, as observed in Figure 1, were constructed in triplicate for each measured temperature in the hydrogenation of benzonitrile. A representative Arrhenius plot is presented in Figure 2 and yields an activation energy of 27.6 kJ mol⁻¹ with a standard deviation on the three measurements of 1.8 kJ mol⁻¹.

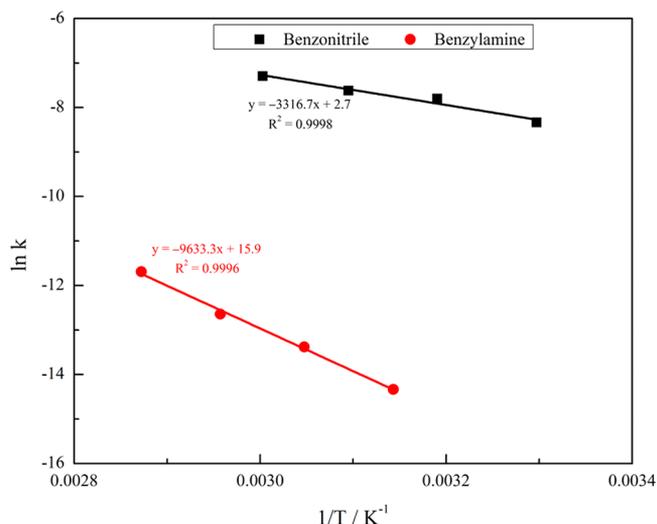


Figure 2. Arrhenius plot for the hydrogenation of benzonitrile (black squares) and the hydrogenolysis of benzylamine (red circles) over a temperature range of 303–333 K, 4 barg, 800 r.p.m. using 500 mg 5 wt % Pd/C catalyst and ca. 17 mmol benzonitrile/benzylamine.

An observed activation energy of 20+ kJ mol⁻¹ typically represents a heterogeneously catalyzed reaction under kinetic control.^{32,33} Nevertheless, at 27.6 kJ mol⁻¹ the activation energy of benzonitrile hydrogenation is closer to the value for diffusion control than would be expected for a well stirred reaction vessel of this nature.¹⁶ This outcome is therefore

suggestive of the presence of a diffusional constraint within the reaction system. Furthermore, a similar study conducted by Hegedüs et al. on the hydrogenation of benzonitrile over a 10% Pd/C catalyst reports two temperature controlled regimes for the activation energy of this reaction.¹² For temperatures below 323 K an activation of 49.8 kJ mol⁻¹ was quoted indicating the absence of diffusional constraints. Conversely, however, diffusional constrictions were observed above 323 K (5.2 kJ mol⁻¹). Somewhat interestingly the activation energy reported in this study, 27.6 kJ mol⁻¹, falls somewhere in the middle of these two values perhaps providing an indication that operation is within a transition regime.¹²

Working on a similar reaction system, Maschmeyer et al. tested for the presence of mass transfer limitations by altering agitation speed and monitoring the effect on the rate of reaction for both benzonitrile hydrogenation and benzylamine hydrogenolysis.¹⁴ While kinetic control was established for the latter reaction at operational agitation, this was not found to be the case for benzonitrile hydrogenation, with diffusion limitations being apparent.¹⁴ These findings indicate the presence of gas-to-liquid mass transport issues which have been shown to be problematic for Pd/C catalysts.^{17,21,24}

For the reaction reported here, however, it was found that increasing autoclave agitation speed did not result in an increase in the benzonitrile hydrogenation rate (section 2.1), indicating an absence of a specific gas-to-liquid mass transfer restriction. Moreover, the initial rate was found to increase linearly with catalyst mass, Figure 3, further reinforcing the absence of gas-to-liquid transport constraints.^{17,21,34} Nevertheless, internal pore diffusion within the carbon support cannot be definitively excluded as a means of providing a mass transfer limitation within the reaction system.

3.1.2. Benzylamine Hydrogenolysis (Liquid Phase): Reaction Order and Energetics. The second stage of the consecutive reaction, benzylamine hydrogenolysis, was likewise considered. The profile for this reaction over the 5 wt % Pd/C catalyst can be visualized in Figure 4. Full benzylamine conversion was achieved within 100 min, selectively yielding the hydrogenolysis product, toluene, and corresponding to a turnover number of 174. On inspection of the reaction profile, toluene formation appears to follow zero-order kinetics, as evidenced by the near linear increase in toluene production with respect to time. The near-quantitative transformation of benzylamine to toluene indicates hydrogenolysis to be a facile process under the conditions reported. The hydrogen uptake curve (blue line) closely follows toluene production. A noticeable mass imbalance is initially observed, but following a similar trend to that seen for benzonitrile hydrogenation, this imbalance is nearly completely recovered at extended reaction times. At the time corresponding to the maximum mass imbalance (ca. 15 min), the ratio of adsorbed species to surface palladium is equal to 34.6. It is thus believed that the origin of the initial mass imbalance is due to adsorption of the amine onto both the Pd surface and the carbon support, causing a momentary retention of this species by the catalyst. As the amine undergoes hydrogenolysis, toluene is released into the liquid phase allowing the mass balance to be recovered by reaction completion.

Figure 5 assesses the suitability of the benzylamine hydrogenolysis reaction to zero-order kinetics. The high linearity of the data over three half-lives indeed indicates a conformation of the hydrogenolysis of benzylamine to zero-order kinetics, with a resultant rate coefficient of 5.74×10^{-4}

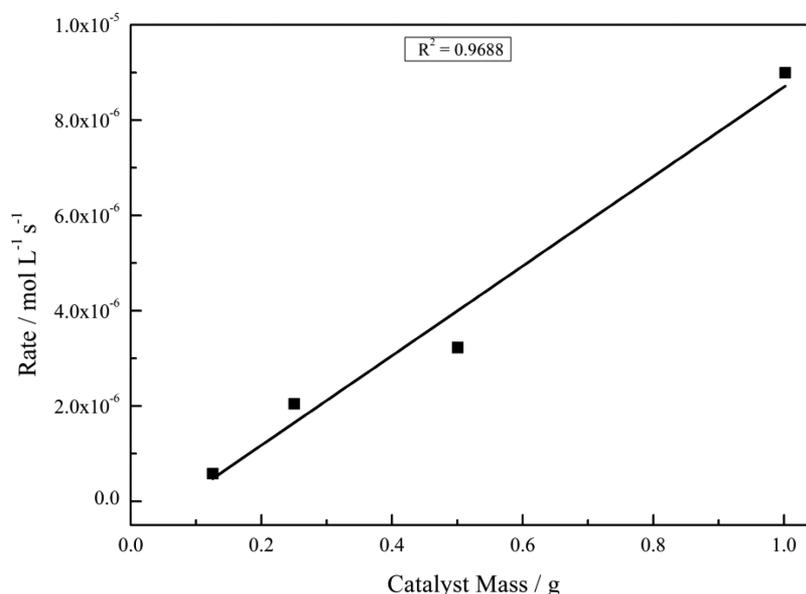


Figure 3. Effect of catalyst mass on the initial rate of benzonitrile hydrogenation at 333 K, 4 barg, 800 r.p.m. over a catalyst mass range of 0.1–1 g using ca. 17 mmol benzonitrile.

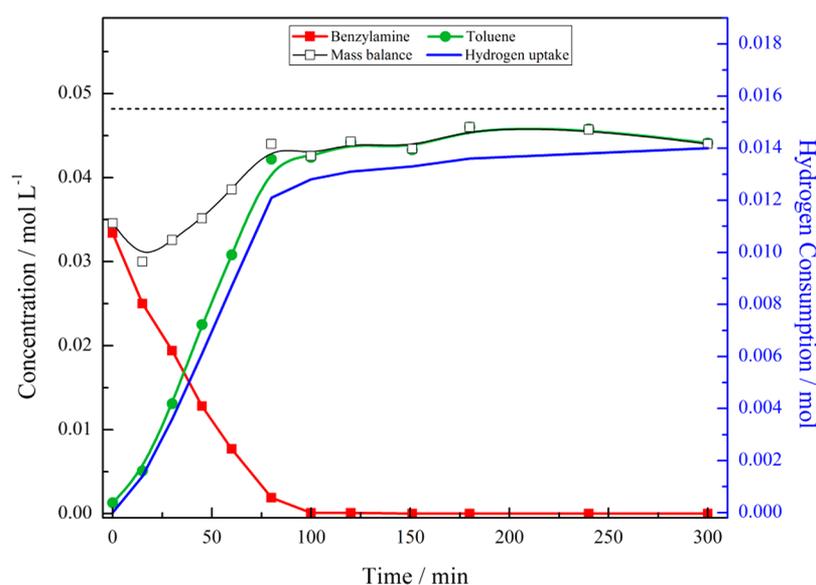


Figure 4. Reaction profile for the liquid phase hydrogenolysis of benzylamine over 500 mg 5 wt % Pd/C, at 333 K, 4.0 barg, 800 r.p.m. and ca. 16 mmol of benzylamine. The dashed line represents the incident concentration of benzylamine.

mol L⁻¹ min⁻¹. Therefore, the direct hydrogenolysis of benzylamine can be expressed as rate = $-d[\text{BA}]/dt = k_2$ where $k_2 = k[\text{BA}][\text{H}_2][\text{catalyst}]$. Here, k_2 represents the observed rate for the transformation of benzylamine to toluene with $[\text{BA}]$, $[\text{H}_2]$, and $[\text{catalyst}]$ denoting the concentration of benzylamine, hydrogen, and catalyst, respectively. As with the hydrogenation of benzonitrile, both $[\text{H}_2]$ and $[\text{catalyst}]$ are constant. However, in addition to this, $[\text{BA}]$ can also be considered as a constant due to saturated binding to the surface. This outcome compares favorably with previous reports on this reaction system by Maschmeyer and co-workers.¹⁴

The Arrhenius plot for benzylamine consumption over a temperature range of 303–333 K is shown in Figure 2. From this plot an activation energy of 80.1 (± 6.4) kJ mol⁻¹ is obtained. The elevated activation energy for this process (cf. E_a

= 27.6 (± 1.8) kJ mol⁻¹ for benzonitrile hydrogenation, section 3.1.1) indicates the establishment of distinct kinetic control in this instance. It is noted that the hydrogenolysis of benzylamine is a single step reaction requiring only 1 equiv of hydrogen. In contrast, the hydrogenation of benzonitrile requires 2 equiv of hydrogen to support a relatively fast reaction that additionally includes a highly reactive imine intermediate. In combination with the reduced hydrogen demand beyond 100% conversion, the slower rate of the hydrogenolysis means that the possibility of mass transport restrictions is less prevalent for this particular reaction step.

3.2. Kinetics of Consecutive Reactions (Liquid Phase, 5 wt % Pd/C): Hydrogenation (First-Order) Followed by Hydrogenolysis (Zero-Order). It has previously been demonstrated that there are two steps, thought to be consecutive in nature, involved in the reduction of

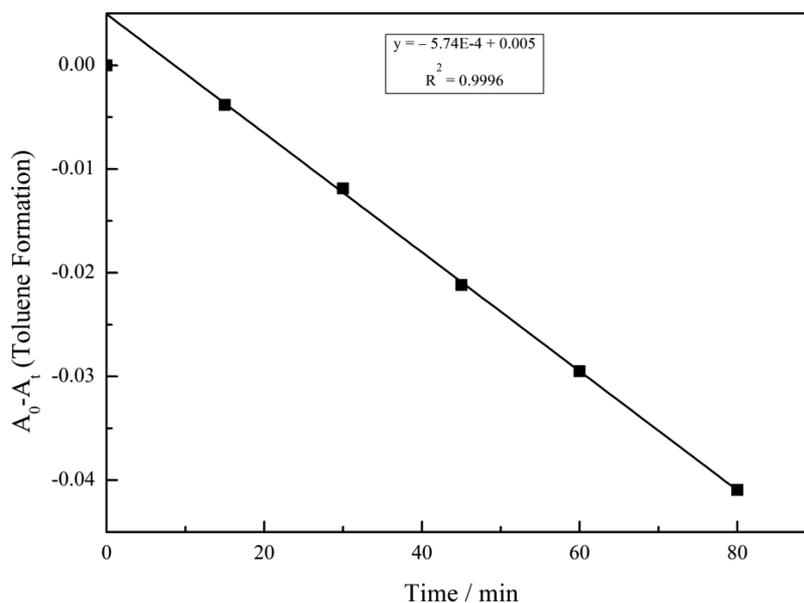


Figure 5. A zero-order plot ($A_0 - A_t$) versus time for benzylamine hydrogenolysis over 500 mg Pd/C catalyst at 333 K, 4 barg, 800 r.p.m. and ca. 16 mmol benzylamine. A_0 and A_t represent initial concentration and concentration at time t , respectively. The linear fit does not include the first data point.

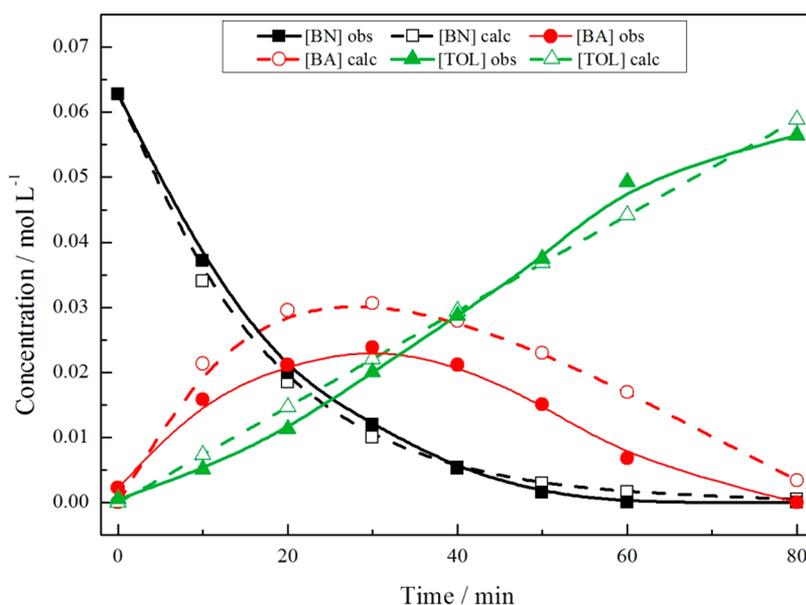
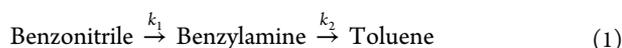


Figure 6. A comparison of the reaction profiles for benzonitrile hydrogenation by experimental means (closed shapes) and by calculation of the kinetic expressions governing a consecutive first to zeroth-order process (open shapes), where [BN], [BA], and [TOL] represent the concentrations of benzonitrile, benzylamine, and toluene, respectively.

benzonitrile: hydrogenation of the nitrile, followed by hydrogenolysis of the amine functionality.⁷ To further investigate the kinetics of the system, the experimentally gained data may be compared with a data fit for kinetic expressions governing a consecutive reaction with a change from first- to zero-order.³⁵ As such, the following sequence may be considered:



,where k_1 and k_2 represent the rate coefficients for the hydrogenation of benzonitrile and hydrogenolysis of benzylamine, respectively. [BN], [BA], and [TOL] represent the respective liquid phase concentrations of benzonitrile, benzyl-

amine, and toluene. Manipulation of the differential forms of the rates of change for both reactant and product gives

$$[\text{BN}]_t = [\text{BN}]_0 e^{-k_1 t} \quad (2)$$

$$[\text{BA}]_t = [\text{BN}]_0 - [\text{BN}]_0 e^{-k_1 t} - k_2 t \quad (3)$$

Subsequent use of the mass balance relationship, where the sum concentration of all reactants and products must equal the initial benzonitrile concentration (A_0), infers that

$$[\text{BN}]_t + [\text{BA}]_t + [\text{TOL}]_t = [\text{BN}]_0 \quad (4)$$

Therefore,

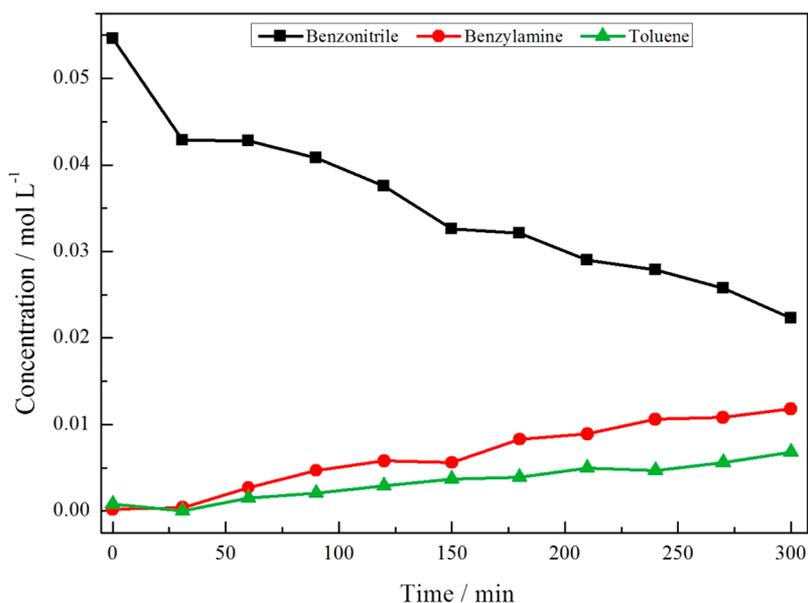
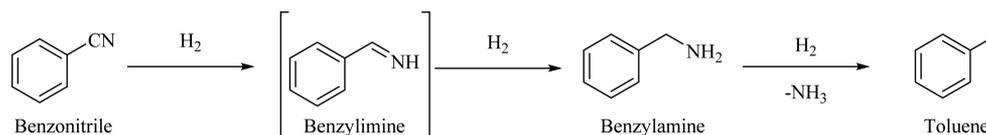


Figure 7. Reaction profile for the liquid phase hydrogenolysis of benzonitrile over 500 mg 1 wt % Pd/Al₂O₃, at 333 K, 4.0 barg, 800 r.p.m. and ca. 17 mmol of benzonitrile.

Scheme 1. Reaction Scheme for the Hydrogenation of Benzonitrile⁷



$$[\text{TOL}]_t = k_2 t \quad (5)$$

Eq 5, describing toluene change over time must, however, be considered with care, as it suggests that the concentration of this species in the system increases without limit. In reality, as visualized in the reaction profile (Figure 4), this is impossible due to the quantity of the product being a finite parameter. Nevertheless, Figure 6 shows that the experimentally obtained data, denoted (*obs*, closed shapes), fit well with the modeled kinetics (*calc*, open shapes).

From Figure 6 it can be seen, as postulated, that the modeled data for toluene formation follow an approximately linear increase at extended times, whereupon it begins to deviate from the experimentally observed profile which begins to plateau. Despite this anomaly that is explained above, the only difference between the experimental and calculated data sets relates to benzylamine concentration. The maximum concentration of this species observed experimentally is consistently low when compared to the modeled kinetic data. This is thought to be due to benzylamine retention by the Pd/C catalyst, as indicated by the momentary mass imbalance at the beginning of the reaction (Figure 4). Nonetheless, a complete mass balance was returned on reaction completion, indicating that product formation was not impeded by this process. Discrepancies between observed and calculated values can also be attributed to the fact that the model takes no account of the imine formation step, vital for amine production, as these species were not detectable in the liquid phase during these experiments.

3.3. PtO₂ and 1% Pd/Al₂O₃ Catalysts (Liquid Phase). Catalyst choice was briefly explored with the aim of further understanding if the mechanistic insights garnered from the 5

wt % Pd/C catalyzed reaction were unique to this catalyst. Two alternative precious metal catalysts, similar to that already used, were hence selected for investigation. First, benzonitrile was hydrogenated over an in-house 1 wt % alumina supported catalyst. From CO chemisorption isotherm data (7.6×10^{18} Pd(s) g_(cat)⁻¹) this Pd/Al₂O₃ catalyst was found to exhibit a metal dispersion of 13.4% corresponding to a mean particle size of 8.3 nm.³⁰ The dispersion quoted for this catalyst is significantly lower than that of the Pd/C reference catalyst (dispersion = 39%, mean particle size = 2.8 nm),⁷ providing the opportunity to assess whether the larger Pd crystallites of the alumina supported catalyst and/or the support material will have an effect on the sequential hydrogenation and hydrogenolysis reactions under consideration.

It is recognized that the rate of a reaction and the product distribution can vary with metal particle size.³⁶ In line with the reduced number of surface Pd atoms, Figure 7 shows the 1 wt % Pd/Al₂O₃ catalyst to have reduced activity when compared to the 5 wt % Pd/C reference catalyst. Indeed, the use of the 1% Pd/Al₂O₃ catalyst afforded a reduced initial TOF (0.113 s^{-1}) when compared to the reference catalyst (initial TOF = 0.234 s^{-1}). Moreover, it was found that the increased particle size of the 1 wt % Pd/Al₂O₃ catalyst did not significantly alter the product distribution, only the rate of reaction. At 50% conversion of benzonitrile, selectivity to benzylamine was 47% for the alumina supported catalyst (cf. 40% selectivity under the same criteria was reported for the 5 wt % Pd/C catalyst). Additionally considered was platinum dioxide (PtO₂), commonly known as Adams catalyst, due to its reported preservation of the amine functionality in the reduction of nitro compounds.^{37,38} Again, a similar profile was obtained with 38% benzylamine selectivity at 50% benzonitrile

conversion achieved over this catalyst. Thus, accessibility of the hydrogenolysis pathway is attainable using both Pd and Pt based catalysts.

3.4. Gas Phase Infrared Spectroscopic Studies. With reference to Scheme 1, the production of toluene is expected to coincide with ammonia formation. However, the latter entity is undetectable in the liquid phase by the available analytical procedures. Given that coincident detection of ammonia alongside toluene formation would provide supporting evidence for a hydrogenolysis stage, the application of gas phase infrared spectroscopic measurements was thought to be informative in terms of confirming the classification of a hydrogenolysis stage. It is noted that, to the best knowledge of the authors, to date and due to analytical constraints, ammonia formation has not been directly determined during the hydrogenation of benzonitrile.

Previous work from this group has established the usefulness of using IR spectroscopy to examine the composition of the gas phase present over a supported metal catalyst operating within a IR gas cell acting as a batch reactor.^{30,31} A similar approach was adopted here to explore the benzylamine hydrogenation reaction, with hydrogenation and deuteration reactions examined over the 1 wt % Pd/Al₂O₃ catalyst. This material was selected in preference to the Pd/C catalyst as its relatively impeded rate of reaction (section 3.4) enabled sufficient spectra of suitable signal-to-noise ratio to be recorded in order to define a complete reaction profile within a time period (*ca.* 30 min) for which the integrity of the cell could be maintained.

The operational temperature of the gas phase IR measurements of 353 K was an experimental compromise. At temperatures in excess of this, overhydrogenation of benzonitrile to yield fully saturated ring structures occurred, while at lower temperatures there was insufficient volatilization, as evidenced by loss of reactant concentration in the vapor phase. Diagnostic bands used for the identification of each compound are presented in Table 1.³⁹ Unfortunately, due to peak overlap, a diagnostic band was not accessible for benzylamine, meaning that an accurate concentration for this compound could not be obtained.

Table 1. Diagnostic Bands Used to Distinguish Each Compound during the Course of the Reaction^a

compound	diagnostic band/cm ⁻¹
benzonitrile	CN stretch at 2238
toluene	CH bend at 729
ammonia	NH wag at 950

^aDue to overlapping peaks, a diagnostic band for benzylamine was not assigned.³⁹

3.4.1. Hydrogenation of Benzonitrile. Figure 8 presents the infrared spectrum in the range 2175–2290 cm⁻¹ as a function of reaction time for benzonitrile hydrogenation over the 1 wt % Pd/Al₂O₃ catalyst at 353 K. At short reaction times, an intense band centered at 2240 cm⁻¹ is evident that is assigned to the CN stretching mode of benzylamine.³⁹ The band progressively diminishes in intensity for increasing reaction times up to ≥25 min, when the feature is no longer present, indicating benzonitrile consumption to be complete about that time. Figure 9 extends the spectral range presented to 400–4000 cm⁻¹ but at a reaction time of 30 min, *i.e.* corresponding to reaction completion.

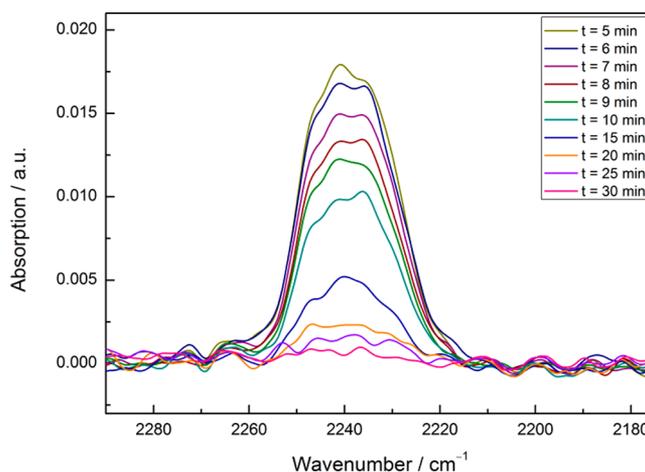


Figure 8. FTIR spectra (2175–2290 cm⁻¹, *t* = 5–30 min) for the gas phase hydrogenation of benzonitrile over 1% Pd/Al₂O₃ at 353 K showing the CN stretch at 2238 cm⁻¹.

Figure 9 shows full conversion of the nitrile moiety, as evidenced by absence of the CN stretch at 2238 cm⁻¹.³⁹ Toluene was produced, confirmed by the presence of the diagnostic CH bend at 729 cm⁻¹, alongside ammonia, demonstrated by its characteristic bands at 950, 1631, and 3444 cm⁻¹.³⁹ The production of these compounds from the benzonitrile hydrogenation reaction confirms the occurrence of the hydrogenolysis reaction.

Figure 10 shows the resultant reaction profile for the hydrogenation of benzonitrile and provides further confirmation that toluene production was indeed coupled with the formation of ammonia. Difficulties were encountered in the determination of an initial concentration for benzonitrile, as a consequence of the hydrogenation rate being faster than the rate of volatilization at 353 K. Nevertheless, since the quantity of reagent added was known, a calculated *A*₀ value is included in the figure. The predicted intensity profile over the first 5 min of reaction is consistent with a first-order decay of benzonitrile as a function of time (section 3.1.1). When the hydrogenolysis of benzylamine was considered, it was again observed that ammonia production coincided with toluene formation. Thus, a hydrogenolysis reaction can be unambiguously associated with the loss of selectivity of benzylamine in the hydrogenation of benzonitrile.

3.4.2. Deuteration of Benzonitrile. From the final IR spectrum recorded at reaction completion for the deuteration of benzonitrile (Figure 11), it can be seen that both toluene-d₃ and ND₃ were formed. Of particular note is the shifting of the band assigned to the CD aliphatic stretch of toluene to around 2170 cm⁻¹ (*cf.* the corresponding CH stretch observed at 2912 cm⁻¹ in Figure 9). Moreover, absence of the CH stretch indicates that toluene-d₃ has been exclusively produced. Shifting of the associated ammonia peaks to lower frequencies has also been observed, accounted for by the deuteration of this species.

The proposed surface chemistry involved in the formation of fully deuterated toluene and ammonia can be visualized in Scheme 2. With reference to Scheme 1, Scheme 2 shows that deuterated benzylamine (C₆H₅CD₂ND₂) is formed as an intermediate species via the corresponding imine. Additionally observed was the preservation of aromaticity under the designated reaction conditions, as evidenced by the maintenance of the CH aryl stretch at approximately 3080 cm⁻¹.

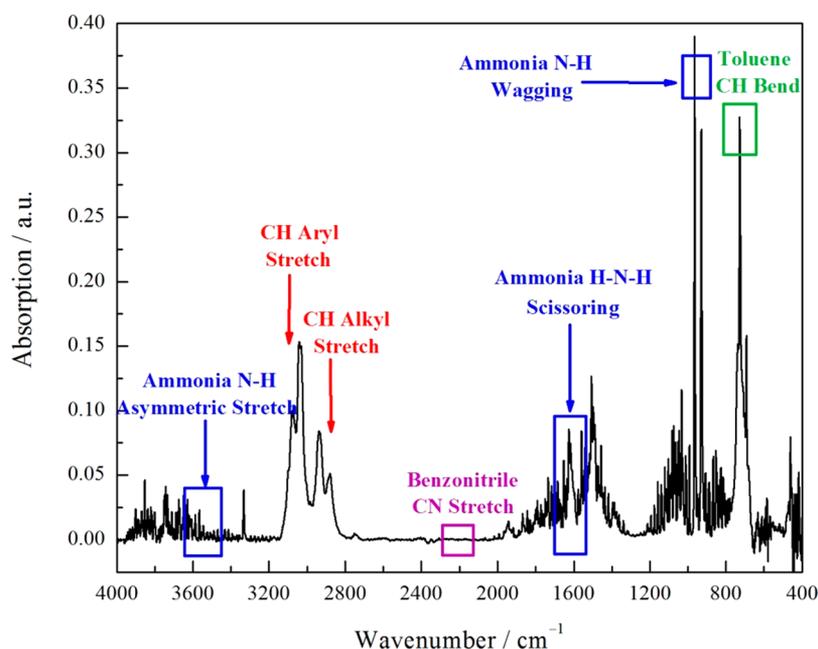


Figure 9. FTIR spectrum (400–4000 cm^{-1}) recorded at $t = 30$ min in the gas phase hydrogenation of benzonitrile over $\text{Pd}/\text{Al}_2\text{O}_3$ at 353 K.

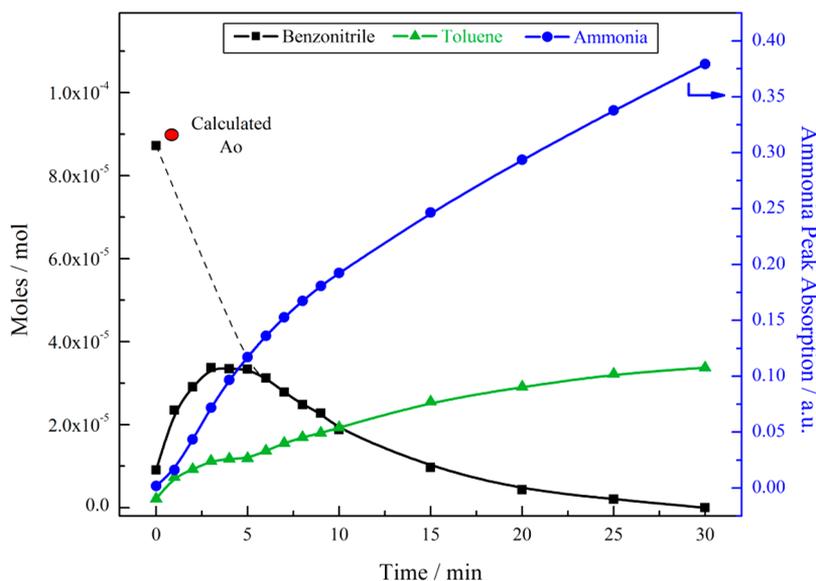


Figure 10. Reaction profile for the gas phase hydrogenation of ca. 0.09 mmol benzonitrile over 500 mg 1 wt % $\text{Pd}/\text{Al}_2\text{O}_3$ at 353 K and 1 bar. The benzonitrile and toluene are presented as moles (left y axis), whereas peak height is used to indicate ammonia concentration (right y axis).

This is therefore indicative of H/D exchange occurring solely at the unsaturated centers external to the ring.

Scheme 2 involves a number of distinct transformations. The benzonitrile first binds through its nitrile functionality and is reduced stepwise, to benzylamine *via* benzylimine. The bound benzylamine can then interact with the surface *via* its aromatic ring where hydrogenolysis can occur.^{40–43} The imine unit is then reduced to produce a surface anchored $-\text{CD}_2-\text{ND}_2$ substituent group. Further deuterium addition leads to coincident toluene- d_3 and ND_3 formation. It is expected that formation of these products leads to a concerted desorption process.

3.4.3. Deuterium Hydrogenolysis of Benzylamine. Investigation of the deuterolysis of benzylamine, **Figure 12**, shows that upon reaction completion it is toluene- d_1 ($\text{C}_6\text{H}_5\text{CH}_2\text{D}$)

which is observed, and not toluene- d_3 ($\text{C}_6\text{H}_5\text{CD}_3$), as was detected for benzonitrile deuteration (**Figure 11**, **Scheme 2**). The production of a nonfully deuterated form of toluene is evidenced, with reference to **Figure 12**, through the presence of both aliphatic CH (2912 cm^{-1}) and CD (2141 cm^{-1}) stretches. A proposed reaction scheme for the formation of toluene- d_1 as a surface process in the deuterolysis reaction is presented in **Scheme 3**.

For the adsorption of benzylamine, the amine unit is thought to bind *via* either the nitrogen lone pair or the aromatic ring to the Pd surface. However, in order for hydrogenolysis to occur, it must be the aromatic ring which is bound to the palladium.^{40–43} Subsequent C–N cleavage leads to an allylpalladium species, which is further deuterated to yield toluene- d_1 and deuterated ammonia.

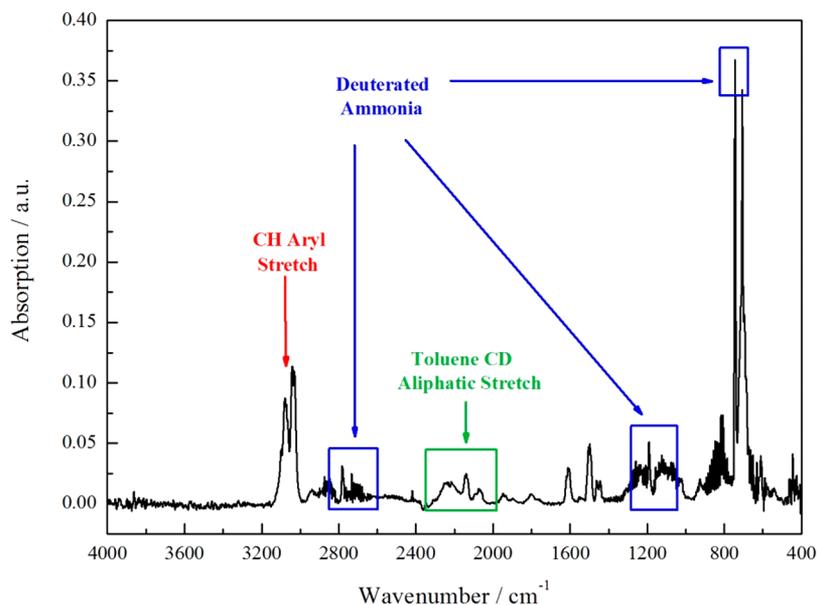
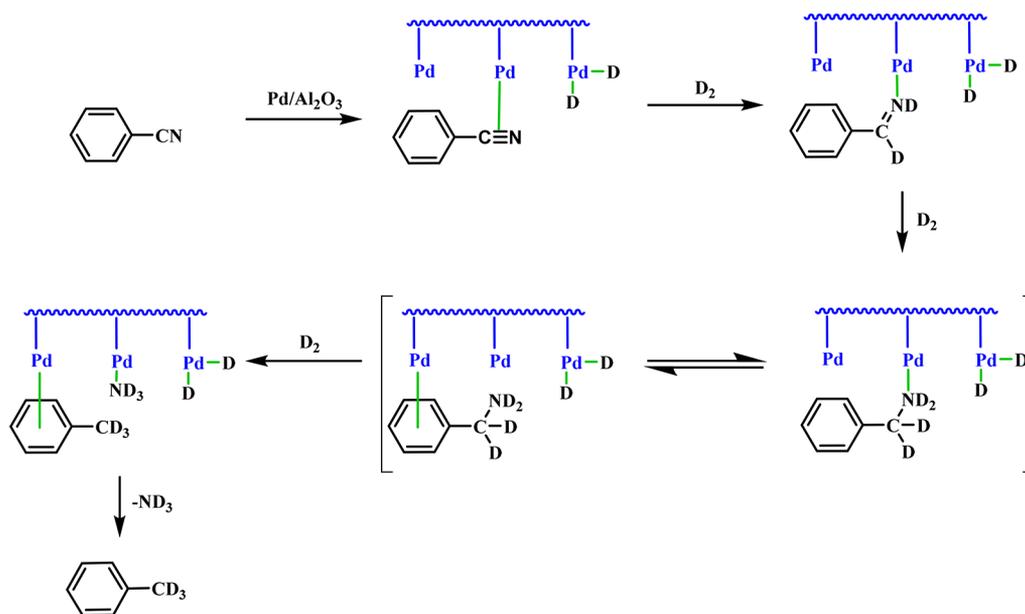


Figure 11. FTIR spectrum ($400\text{--}4000\text{ cm}^{-1}$), recorded at $t = 30\text{ min}$, for the gas phase deuterium hydrogenation of benzonitrile over 1 wt % Pd/Al₂O₃ at 353 K.

Scheme 2. Proposed Reaction Scheme for the Deuteration of Benzonitrile over an Alumina Supported Pd Catalyst Resulting in the Formation of Toluene-d₃



It was assumed that, alongside toluene-d₁, NH₂D would be observed. However, only the fully deuterated form of ammonia (ND₃) was detected experimentally. The simultaneous formation of partially deuterated toluene and fully deuterated ammonia provides an indication that these processes are decoupled from each other. It is therefore suggested that ND₃ must be produced as the result of a hydrogen exchange process: NH₃ + xD₂ ⇌ ND₃ + H₂ (with x indicating an excess of D_{2(g)}). Exclusive formation of this species indicates that this reaction is fast, is Pd catalyzed, and, in this case, effectively makes the ammonia production *unselective*. Theoretically it should be possible to use ammonia isotopomers, distinguishable by IR spectroscopy,⁴⁴ to probe the adsorption geometry linked with the benzylamine hydrogenation process. For this

particular application, however, this information was not accessible as a consequence of the rapid nature of the H/D exchange under the designated reaction conditions.

The other product of the reaction, toluene-d₁, was identified by the presence of both CH and CD aliphatic stretches. Nevertheless, care is required in the interpretation of these results. The presence of both CH and CD stretches in the IR spectra infers only that toluene-d₃ is not exclusively formed. As a consequence, the presence of both toluene-d₂ and toluene-d₃ alongside toluene-d₁ cannot be excluded. As with the rapid H/D exchange observed in ammonia formation, it is possible that the bound toluene-d₁ may also undergo H/D exchange resulting in formation of toluene-d₂ and toluene-d₃. Due to detection of a toluene CH bond it can be deduced that H/D

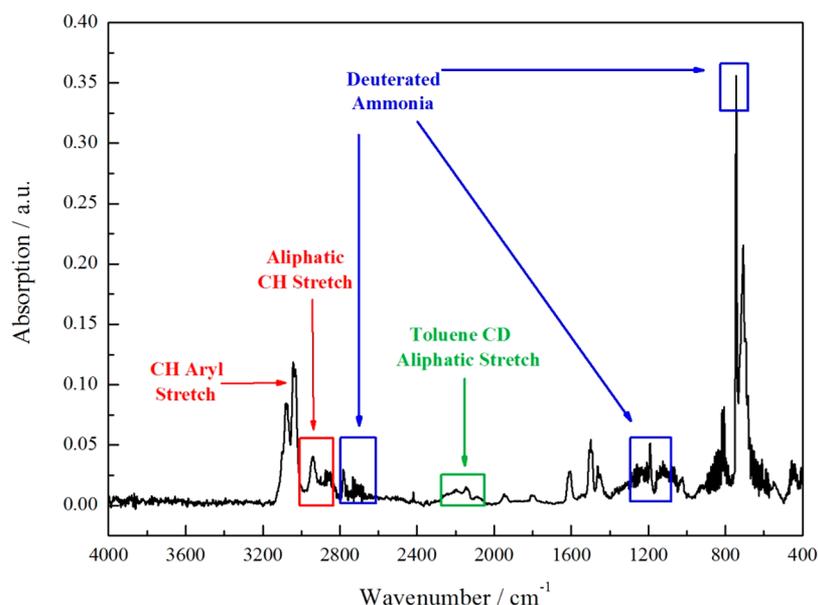
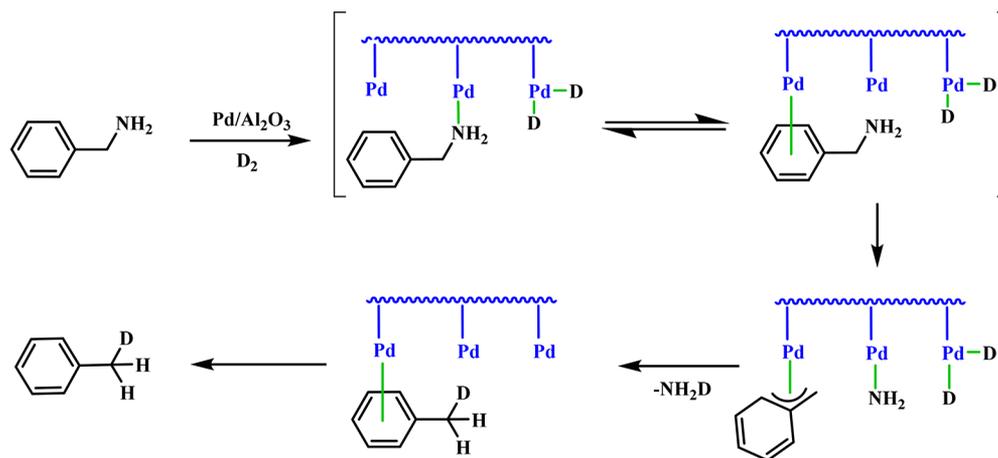


Figure 12. FTIR spectrum ($400\text{--}4000\text{ cm}^{-1}$), recorded at $t = 30\text{ min}$, for the gas phase deuterium hydrogenolysis of benzylamine over $\text{Pd}/\text{Al}_2\text{O}_3$ at 353 K . Of note is the presence of both the aliphatic CH and CD stretches in the spectrum.

Scheme 3. Proposed Reaction Scheme for the Direct Deuterolysis of Benzylamine Resulting in Formation of Toluene- d_1



exchange for this species is not fast. Thus, while deuterium incorporation to form toluene- d_2 and toluene- d_3 cannot be ruled out, nevertheless, it is shown to be a slow process when compared to the ammonia exchange.

As a consequence of the gas phase reaction conditions, there is also the potential for an additional method of deuterium enrichment. Scheme 1 shows that, as with all nitrile hydrogenations, amine formation is preceded by an imine intermediate. Taking into account the reversible nature of this process, Maschmeyer et al. proposed that this could provide a route “back” from the amine to the imine, a process that would allow further deuteration of the toluene to be achieved.¹³ The implication is thus that for benzylamine the direct deuterolysis to yield toluene- d_1 is now in competition with the “back” reactions which allow toluene- d_2 and toluene- d_3 to be produced.

4. CONCLUSIONS

The heterogeneously catalyzed liquid phase hydrogenation of benzonitrile has been considered. Analysis of the hydrogenation and hydrogenolysis pathways which resulted in

formation of toluene allowed the interconnectivity of the two reactions to be assessed. When separately considered, benzonitrile hydrogenation and benzylamine hydrogenolysis were found to have differing kinetics and energetics. The hydrogenation of benzonitrile followed first-order reaction kinetics with a corresponding activation energy of 27.6 kJ mol^{-1} . Contrastingly, the hydrogenolysis of benzylamine not only had a much higher activation energy (80.1 kJ mol^{-1}) but also exhibited an overall zero-order dependence. Use of alternative catalysts to improve the selectivity to the desired product were investigated, though these were found to be inferior in performance compared to the reference 5 wt % Pd/C catalyst.

Gas phase studies performed over a 1 wt % $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst showed that the hydrogenation of benzonitrile and benzylamine follow a similar trend with toluene production coinciding with ammonia formation. The corresponding deuteration of both species, however, yielded different products. Deuteration of benzonitrile resulted in the formation of exclusively toluene- d_3 and ND_3 with deuterium addition occurring at the unsaturated centers external to the aromatic

ring. Contrastingly, a CH stretch alongside the CD stretch was observed in the deuteration of benzylamine indicating formation of toluene which was not fully deuterated as well as fully deuterated ammonia. A H/D exchange process resulting in a mix of toluene products for the hydrogenolysis cannot be excluded. Nevertheless, this H/D exchange is slow when compared to the rapid scrambling required to achieve the exclusive formation of ND₃.

The unambiguous detection of evolved ammonia confirms the presence of a hydrogenolysis reaction in the benzonitrile system over a supported Pd catalyst. This distinct chemical transformation is the cause of the dramatic loss in selectivity to benzylamine. The work provides some insight into the interconnectivity of hydrogenation and hydrogenolysis for the reagents studied.

AUTHOR INFORMATION

Corresponding Author

*E-mail: David.Lennon@glasgow.ac.uk. Telephone: (+44)-(0)-141-330-4372.

ORCID

David Lennon: 0000-0001-8397-0528

Notes

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