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University
of Glasgow

HYDROGENATION OF ALKENYL NITRILES

A thesis submitted for the degree of MSc

**University of Glasgow
Department of Chemistry**

**FERAS ALSHEHRI
2012**

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I declare that this thesis is the result of my own work except where due reference is made to other authors. It has not been submitted for any other degree at the University of Glasgow or any other university.

Signature_____

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1. Abstract:

Four isomeric, unsaturated nitriles were hydrogenated, separately and as mixtures, over a Pd/alumina catalyst in a three-phase system at various pressures and temperatures. The nitriles were allylcyanide, cis- and trans-crotonitrile and methacrylonitrile and all have the general formula C_4H_5N . By varying hydrogenation conditions (temperatures, hydrogen pressure and substrate concentrations) activation energies and reaction orders were determined. Allylcyanide had the lowest activation energy because of the stability of its structure (non-conjugated) compared to the other substrates (conjugated). Reaction orders were -1, 0.5 and 1 for allylcyanide, crotonitrile and methacrylonitrile respectively. These findings indicate a difference in the strength of adsorption of each reactant, where allylcyanide is strongly adsorbed to the catalyst surface and methacrylonitrile weakly adsorbed. Isomerisation, which usually accompanies double bond hydrogenation in alkenes, was not observed. This lack of isomerisation may be due to the presence of more than one unsaturated group and the lack of an appropriate acid/base site on the support.

A range of different solvents were used to identify solvent effects for every isomer. A full kinetic analysis involving activation energies and reaction orders was undertaken for IPA and 1-propanol. An effect on reaction orders was observed and was believed to be related to competitive adsorption by the solvent. The activity of the system was sensitive to solvent and reactant. No single solvent parameter could be shown to trend with the variations observed. Variation of conversion in different solvents was related to substrate structure.

Competitive hydrogenation revealed subtle differences between the isomers. Allylcyanide did not show a significant change in reactivity when reacting in the presence of other isomers possibly because of it being more strongly adsorbed or because it adsorbed on corner or edge sites. Both crotonitrile and methacrylonitrile had their reactivity reduced in the presence of allylcyanide and when competing against each other. The behaviour was in keeping with the understanding developed for alkene hydrogenation over palladium.

2. Introduction:

The definition of a catalyst has evolved since Berzelius first invented the term in 1836 [1] but the fundamental concepts have not changed. Generally, a catalyst is considered to be substance that will increase the rate of a chemical reaction without becoming used up during the process. A catalyst can increase the rate of a chemical reaction and speed its attainment of equilibrium, however the reaction thermodynamics cannot be changed and neither can the thermodynamic equilibrium position be altered. Catalysts can take any physical form and are known as homogenous catalysts if they are in the same state as the reagents in the reaction it is promoting, or heterogeneous if in a different state. Heterogeneous catalysts usually consist of small metal particles dispersed across an inert support material such as alumina or silica [2]. The use of a support helps to increase the metal surface area and also leads to increased thermal stability. The use of catalysts in industry is wide spread with approximately 90 % of industrial products encountering a catalyst at some point in their synthesis [3]. Therefore, the area of catalysis is of vital importance to the modern economy and for future industrial developments where existing processes need to be improved for economic or environmental reasons.

Catalytic hydrogenation reactions are widely carried out in industry, from large scale processes in refineries to small batch processes in the pharmaceutical industry. Hydrogenation is one of the reduction reactions. It involves the addition of hydrogen to unsaturated multiple bonds (such as C=C, C≡C, C=O and C≡N) after breaking down these bonds by a catalyst under selected reaction conditions [4]. In 1899 Sabatier and Senderence succeeded in hydrogenating unsaturated compounds to their corresponding saturated compounds over a nickel based catalyst. This work won Sabatier the Nobel Prize in 1912 [5]. Since then, heterogeneous catalytic hydrogenation has become one of the most important reactions for producing pharmaceuticals, nutraceuticals, flavours and fragrances, agrochemicals and fine chemicals [6]. Selective hydrogenation reactions are also widely used, for example in the industrial polymerization process for the elimination of alkynes and dienes from gas streams that contain high amount of alkenes [7].

Catalytic hydrogenation is usually carried out using heterogeneous catalysts because of the catalyst stability and the fact that products are separated easily. Table 1 shows different hydrogenation reactions and the catalysts used in these reactions. Most of the metals used for hydrogenation are from group VIII (Fe, Co and Ni groups). Their usage depends on the nature of the reaction.

Table 1- Examples on hydrogenation processes and catalysts used [4].

Process	Catalyst
Hydrogenation of alkenes	supported Ni, Cu, Pt, Pd, Ru and Rh
Hydrogenation of alkynes	supported Ni, Pd, Ni-Pd, Co-Pd, and Cu-Pd
Hydrogenation of aromatic hydrocarbons	supported Ni, Pd, Rh, Pt and Co-Mo, Raney Ni
Hydrorefining of motor fuels	Ni, Ni-Mo, and Co-Mo on Al ₂ O ₃ and kieselguhr
Hydrogenation of nitriles	supported Ni, Pd, and Pt
Hydrogenation of carbonyl compounds	skeletal and supported Ni and Co, supported Pd, Rh, and Pt and Cu-Cr-O, Cu on kieselguhr
Hydrotreating (hydrodesulfurisation)	Ni-Mo, Ni-W, Co-Mo, Co-W, and Ru on Al ₂ O ₃ and carbon, Mo and W carbides
Hydrogenation of CO and CO ₂ (methanation)	supported Ni, Cu, Co, Fe, Pt and Rh, Pt mesh, Mo and W carbides

Nickel and palladium are used widely in hydrogenation reactions because they adsorb and dissociate hydrogen easily. Other metals such as iron and copper are less used because they have a poorer interaction with hydrogen [8].

It is important to consider general concepts in the field of hydrogenation before carrying out hydrogenation reactions in the lab or on industrial scale. These concepts, which include choosing the catalyst, support, reactor and other reaction conditions (solvent, temperature, and H₂ pressure) are discussed by Paul N. Rylander in two textbooks [9] [10].

Supported noble metals (palladium, platinum, ruthenium and rhodium), supported Ni and Cu and Raney type catalyst are known as classical hydrogenation catalysts [11]. It is widely known that many metals show high activity in the hydrogenation of the carbon-carbon double and triple bonds [7]. The metals mostly used for hydrogenations are palladium, platinum and nickel. Almost all metals listed in table 1 can be prepared with a large surface area, which is an important factor in the hydrogenations reactions because

activity is directly related to active surface area [12]. Palladium is known as a suitable metal for C=C double bond hydrogenation [13]. It is also known to be one of the most used catalytic metals for obtaining partial hydrogenated products [14] or semi hydrogenations [7]. It is widely used in hydrogenating organic fine chemicals and aromatics, petroleum refining and selective hydrogenation of acetylene to ethylene [15].

The primary role of a support material is to disperse the active phase providing a larger surface area and therefore improving the catalytic ability of the active phase. In addition, support material also provides mechanical strength, thermal stability and gives the catalyst its shape. Support materials are often highly porous solids with very high surface areas, such as alumina ($< 300 \text{ m}^2\text{g}^{-1}$), silica gel ($< 800 \text{ m}^2\text{g}^{-1}$) or activated carbon ($< 1000 \text{ m}^2\text{g}^{-1}$). The support material used in this study was θ -alumina. Alumina typically has a surface area of $1\text{-}300 \text{ m}^2\text{g}^{-1}$. Alumina supports can be made by thermal dehydration of $\text{Al}(\text{OH})_3$ (Gibbsite or Bayerite) or AlOOH (Boehmite). Figure 1 shows the different forms of alumina, the starting materials used to form the different types and the characteristics for each type. It also shows the temperatures at which the different types of alumina will experience a phase change and the type of alumina that would be formed.

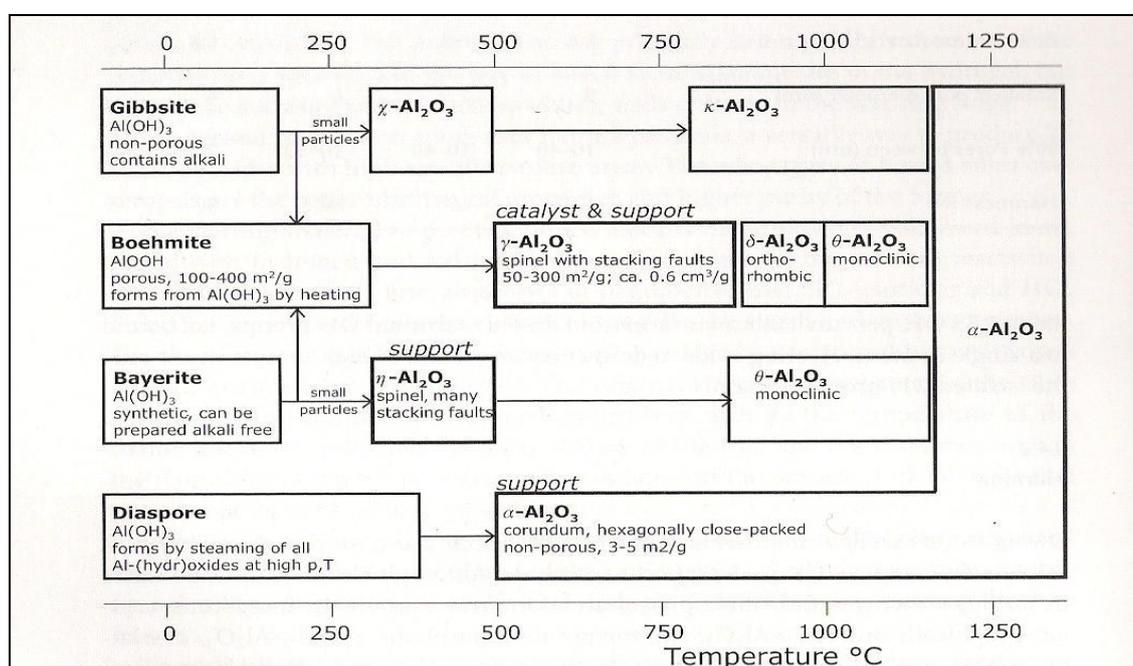


Figure 1- Different forms of alumina

2.1 Reaction Parameters:

Hydrogenation reactions are influenced by several factors including temperature, H_2 pressure, solvent, substrate concentration and catalyst weight [16]. These effects can

affect selectivity and reaction kinetics [17]. These aspects can be of a physical nature such as hydrogen solubility or solvent viscosity or of a chemical nature, which may affect adsorption, desorption, activation energy and surface coverage.

A general liquid phase catalytic hydrogenation process (figure 2) was described by Cerveny and Ruzicka [18] as follows:

- a- Hydrogen is absorbed by the solvent.
- b- External diffusion, where hydrogen and reactant are dispersed through solvent to the catalyst surface.
- c- Internal diffusion, where hydrogen and reactant are dispersed through the catalyst pores.
- d- Reactants are adsorbed on the catalyst surface.
- e- Reaction between adsorbed reactants and compounds in the bulk phase.
- f- Diffusion of the product into the bulk phase after desorbed from the catalyst surface.

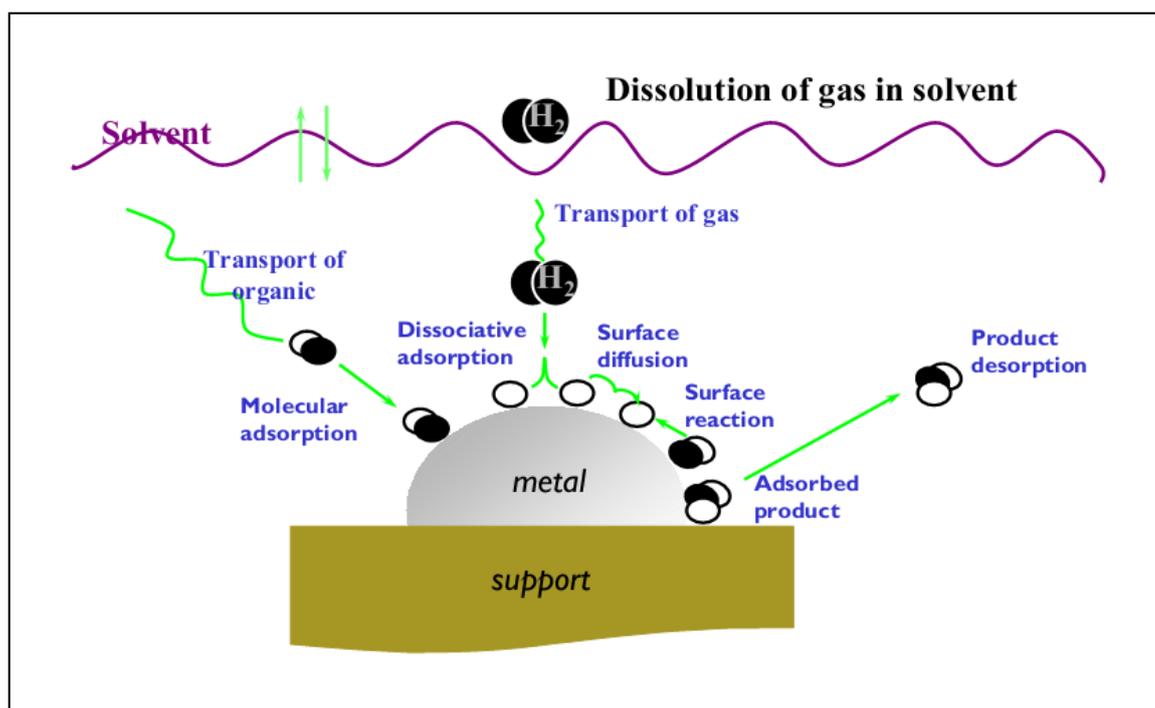


Figure 2- Representation of liquid phase hydrogenation.

2.1.1 Solvent Effect:

Liquid phase hydrogenations may be carried out in solvents such as alcohols, ethers or hydrocarbons. Their role includes dissolving reactants and products, controlling reaction exothermicity, and dissolving site blockers (reaction by-products) from the catalyst surface [19]. Solvents can affect the reaction either chemically or physically, which can

influence the reaction rate and selectivity. An example of a chemical effect is when solvent molecules and substrate or products are coadsorbed on the surface competitively, while physical effects would include hydrogen solubility and viscosity [16]. Both chemical and physical effects were mentioned by Rajadhyaksha and Karwa [20]. They investigated the hydrogenation of *o*-nitrotoluene over Pd/C catalyst in different solvents such as methanol, isopropanol, isobutanol, hexane and benzene. They attributed the solvent effect to (a) the different solubility of H₂ in the solvents, (b) competitive adsorption of solvents on the active sites of the catalyst, and (c) interaction between solvent molecules and reactant and product molecules. They also observed changes in the activation energy when the medium of the reaction was changed.

Kishida and Teranishi [21] investigated different solvents (hexane, cyclohexane, methanol and isopropyl alcohol) in the liquid phase hydrogenation of acetone over Raney nickel and found that the solvents were competitively adsorbed on the surface of the catalyst. Gamesz *et al.* [22] hydrogenated ethyl pyruvate over Pt/Al₂O₃ in different solvents (toluene, ethanol and propylene carbonate). They found that the medium of hydrogenation had an effect on adsorption and desorption processes, which led to changes in the kinetics of the reaction. Augustine and Techasauvapak [23] studied the effect of solvent on the hydrogenation of 4-methyl-1-cyclohexene over Pt/SiO₂ and using pentane, ethyl acetate, THF and methanol as solvents. They found that the adsorption process may be affected because of the interaction between solvent molecules and the metal. The solvent interaction with catalyst and substrate can also be responsible for effecting the kinetics of liquid phase hydrogenation [24]. Augustine *et al.* suggested that methanol was adsorbed on active Pd catalysts, resulting in it occupying the active sites on the catalyst surface instead of hydrogen [25]. Toukoniitty *et al.* stated that rate of hydrogenation reaction was decreased when solvent was present on the surface and when it interacted and competed with reactants especially in the case of solvent at high concentration [26]. Panpranot *et al.* [27] reported that high polarity solvents often compete with the substrate on a catalyst surface leading to a decrease in catalyst activity. Cerveny and Ruzicka [18] declared that solvents have a significant effect on selectivity when hydrogenating two substrates with different structure such as olefins and unsaturated alcohol, while in the case of hydrogenating a substrate with a similar structure, such as cyclohexene and 1-hexene, solvents have a minor effect on selectivity. Acidity, polarity and dielectric constant of the reaction medium can also have an influence on liquid phase hydrogenation.

2.1.2 Effect of pressure and temperature:

In general hydrogenation reactions result in a reduction in reaction volume hence an increase in pressure tends to increase rate. Nevertheless the rate of hydrogenation can also be affected by hydrogen pressure due to several other factors such as catalyst, substrate and reaction conditions. For example, Adkins [28] stated that the hydrogen pressure applied is governed by the type of catalyst used, citing the examples of Pd and Pt that are active at atmospheric pressure whereas Cu requires a higher pressure to be active for hydrogenation reactions. Unsaturated molecules such as alkenes, alkynes and nitriles adsorb strongly on metal catalysts and hence have zero or negative order kinetic terms. On the contrary hydrogen is less strongly adsorbed and is usually found to have a positive order therefore for most reactions the rate of hydrogenation is increased and time of reaction is reduced with the increasing of H₂ pressure [29] [30].

The effect of increasing temperature in a catalytic reaction can have effects on both thermodynamics and kinetics. In general hydrogenation reactions are exothermic hence increasing the temperature will be unfavourable thermodynamically. The kinetic effect is described by the Arrhenius equation, $k = A \cdot \exp(-E_a/RT)$ where k = the rate constant, A = the pre-exponential factor, E_a = the activation energy, R = the gas constant and T = temperature in Kelvin, so that as temperature is increased the rate constant increases. At low temperatures (< 100°C) the kinetic effect vastly outweighs any thermodynamic effect.

Singh and Vannice [31] studied the hydrogenation of ethylene and found that the reaction had a zero order dependence on ethylene at low temperatures and a negative order at higher temperatures, whereas the hydrogen order dependence was 0.5 at low temperature but changed to 1.1 at higher temperatures. They attributed this to the increase in the number of sites available for competitive adsorption after desorption of ethylene at higher temperatures.

Kalantri and Chandalia [32] tested the kinetics of the o-nitroaniline hydrogenation over Pd catalyst using methanol as the solvent. They varied the temperature applied to the reaction from 47°C to 74°C and they found a major increase in the rate with the increase in temperature. In addition, the reaction was a zero order with respect to hydrogen and first order with respect o-nitroaniline.

2.2 Mechanism

In some hydrogenation reactions where there are multiple functional groups one of these functional groups may be preferentially hydrogenated. This type of reaction is called regioselective. In addition, regioselectivity can occur on conjugated systems where a hydrogen atom is added to one position of the conjugated system [16]. Guo and Madix [33] hydrogenated 1,3-butadiene over Pd at 300 K and they did not observe the formation of butane in their results. They found that on hydrogenation of one C=C bond in butadiene over Pd, butene is forced to desorb from the surface of the catalyst by unreacted butadiene, which is more strongly adsorbed, preventing further hydrogenation to butane. Ouchaib and Massardier [34] stated that on a Pd surface butadiene is adsorbed more strongly than butene which leads to desorption of butene, whereas with Pt, butadiene and butene have similar heats of adsorption and so butene remains adsorbed on the surface resulting in the formation of butane.

Hydrogenating C≡N in the presence of C=C in an unsaturated nitrile, may result in saturated nitriles, saturated amines and unsaturated amines. Factors such as functional group proximity or conjugation can affect which group is hydrogenated first, with short chain unsaturated nitrile or conjugated systems the C=C double bond should be hydrogenated preferably from a thermodynamic point of view [35, 36]. On the other hand, in the case of hydrogenating long chain nitriles or when the double bond is sterically hindered the hydrogenation of the double bond is slower [36]. Singh and Vannice stated that isolated or non-conjugated C=C double bonds hydrogenated easier than conjugated C=C [31]. Schäringer *et al.* [37] investigated the co-hydrogenation of acetonitrile and butyronitrile over Raney-Co. They found that acetonitrile was hydrogenated faster than butyronitrile because it was more strongly adsorbed on the surface of the catalyst.

As stated earlier, hydrogenating unsaturated nitrile may result in saturated nitriles, saturated amines and unsaturated amines. Therefore the hydrogenation mechanism of the unsaturated groups will be discussed separately.

2.2.1 C=C double bond reduction:

In order to understand olefins hydrogenation the simplest olefin ethylene has been used as reaction model. It has been used for more than seven decades [38]. The mechanism of ethylene hydrogenation is affected by the location of the active sites as well as the

reaction conditions. Hydrogen and ethylene can be adsorbed and compete for the same surface sites or they can be adsorbed separately [39].

In 1934 [40] Horiuti and Polanyi proposed their famous mechanism (figure 3) which became widely used in text books as well as in academic discussions.

Mohsin *et al.* [41] and Neurock and van Santen [38], summarised three major mechanisms that were suggested for ethylene hydrogenation; a) the Horiuti and Polanyi mechanism which involves chemisorption of ethylene on metals by breaking one of the double bonds between the carbon atoms forming a di- σ -bonded ethylene, which is then hydrogenated to an ethyl species before forming ethane [42], b) the Farkas and Farkas mechanism which involves a dehydrogenation reaction of the ethylene before it is hydrogenated to ethane and c) the mechanism proposed by Zaera and Somorja where an ethylidyne ($C\equiv CH_3$) is formed as an intermediate to transfer hydrogen to the adsorbed ethylene.

Navalikhina and Krylov [4] investigated the mechanism for the hydrogenation of $C=C$ and other functional groups on number of catalysts based on nickel and the noble metals. They declared that a number of adsorbed alkenes were competing with hydrogen for the active sites. They found that weak bonds of the π type are more likely to be hydrogenated at relevant low temperatures.

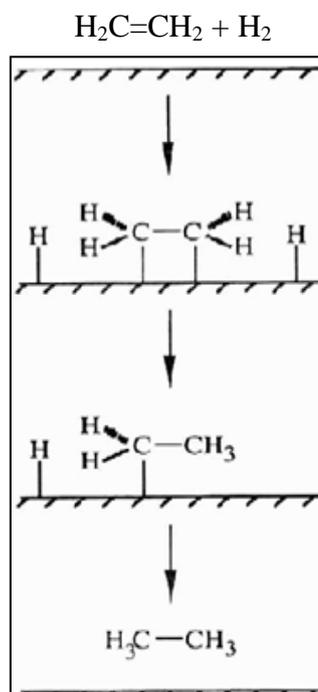


Figure 3- Hydrogenation of ethylene according to the mechanism proposed by Horiuti and Polanyi [43]

2.2.1.1 Mechanism and surface species:

During ethylene hydrogenation several intermediates could be formed, such as ethylidyne and/or other C_xH_y species [42]. Cremer *et al* [42] studied ethylene hydrogenation *in situ* using infrared-visible sum frequency generation (SFG) to monitor the surface vibrational spectrum. They used Pt(111) as a catalyst under 1 atm of gas at 259 K. The following species were observed on the surface in various amounts depending on conditions: ethylidyne [44], di- σ -bonded ethylene, π -bonded ethylene [45], and ethyl groups. Van Santen and Neurock stated that the major species that adsorb on the metal surface during ethylene hydrogenation are di- σ and π -bonded ethylene [45]. The di- σ adsorbed form is where ethylene interacts with two metal atoms and the π adsorbed type where ethylene interacts with a single metal atom [46]. All these forms are shown on figure 4.

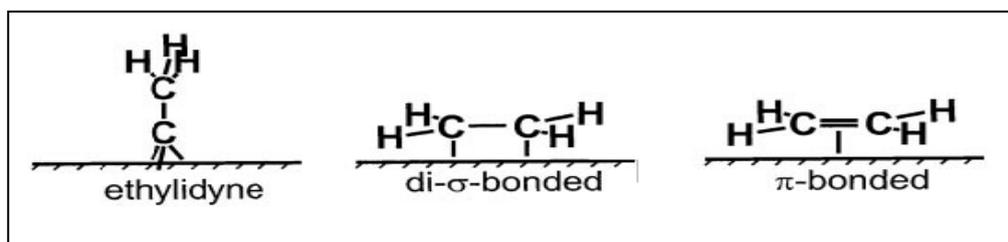


Figure 4- Forms of ethylene adsorbed on the surface during ethylene hydrogenation [47]

According to Cremer *et al* [42], π -bonded ethylene is formed below 52 K. This π -bonded species converts, if it is heated above 52 K, to the di- σ -bonded ethylene (two σ bonds) which dehydrogenates to ethylidyne at a temperature above 240 K, where a hydrogen moves to one of the two carbons.

Beebe *et al.* [48] made an *in situ* study of the hydrogenation of ethylene over Pd/Al_2O_3 by using transmission infrared spectroscopy. They concluded that ethylidyne was not an important species for the ethylene hydrogenation process. It was suggested that ethylidyne was a 'spectator species' which means that the hydrogenation rate is independent of the existence of ethylidyne. This conclusion was also supported by Davis *et al.* [49] and Rekoske *et al.* [50].

Mohsin *et al.* [41] studied ethylene hydrogenation and adsorption on Pt/Al_2O_3 by using FTIR. They found that ethylene was adsorbed as di- σ -ethylene, π -ethylene and ethylidyne. They declared that π -adsorbed ethylene was responsible for ethylene hydrogenation. Cremer *et al.* [42] also came to the conclusion that π -bonded ethylene

species was the essential intermediate for ethylene hydrogenation to ethane, even when the surface was covered di- σ ethylene species.

2.2.2 C₄ hydrogenation and isomerisation:

With olefins larger than C-3 there are side reactions that might accompany hydrogenation such as double bond migration and cis-trans isomerisation. Double bond migration and cis-trans isomerisation are shown in figure 5.

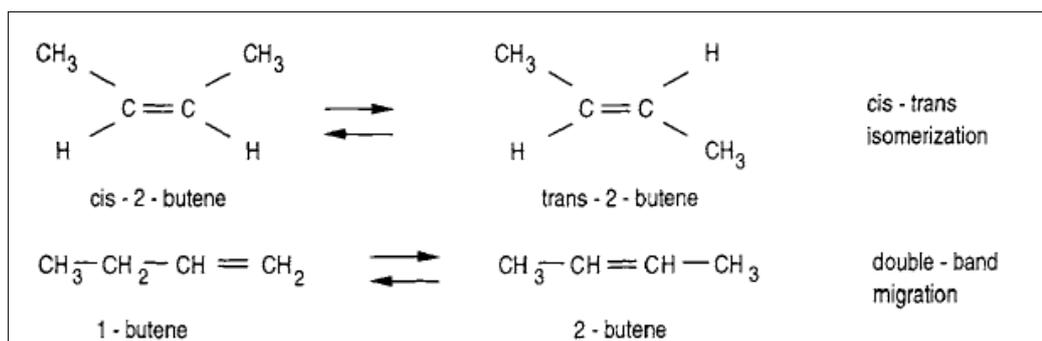


Figure 5- Reactions accompanied olefins hydrogenation [51].

Smith and Notheisz stated in their review [52] that during hydrogenation of C=C double bonds cis/trans isomerisation may occur. They said the isomerisation is a structure dependent reaction and is controlled by kinetics and thermodynamics, with the less stable double bond isomerised to the more stable one. The movement of the double bond on the carbon chain is proposed to occur through a half hydrogenated state, which is supported by experiments. However isomerisation may be inhibited or not occur when the olefin contains additional functional groups.

Isomerisation of alkenes is usually an undesired side reaction that accompanies double bond hydrogenations that are catalyzed by transition metals. It is more likely to occur in the case of low hydrogen pressure. Hydrogenation involves adsorption of alkene and hydrogen on the catalyst surface (figure 6). Hydrogen then can move to the adsorbed alkene to form a metal-alkyl then alkane is formed. All these steps are reversible (except the last one) which may lead to isomerisation [53].

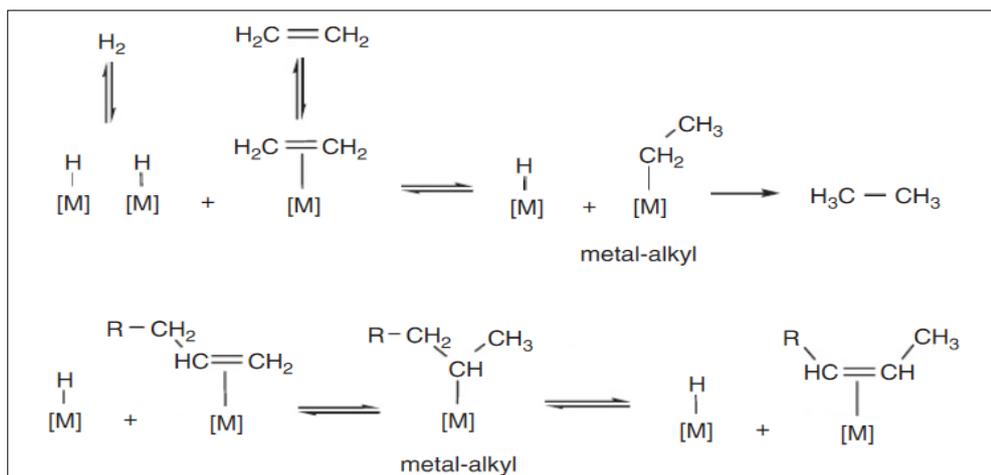


Figure 6- Hydrogenation and isomerisation mechanisms [53].

Musolino *et al.* [54] hydrogenated *cis*-2-butene-1,4-diol at 303 K at atmospheric pressure. They tested Pd, Pt, Ru, Rh and Ir supported on silica. They found that the hydrogenation reaction was preferred when Pt and Ir were used. The isomerisation was detected when Pd, Ru and Rh were the catalysts. They concluded that hydrogen elimination is a fundamental stage in the process leading to isomerized olefinic products and that it competes with hydrogen transfer to hydrogenated compounds.

As stated earlier alkene hydrogenation over Pd is considered a structure insensitive reaction. However, Hub *et al.* [55] found that the hydrogenation of 1-butene and 1-butyne over Pd/Al₂O₃ was affected to some extent by varying the dispersion of a palladium on alumina catalyst. They found that the turnover number was increased with increasing the dispersion of palladium (small particle size). In addition, Shaikhutdinov *et al.* [47] also found that the adsorption of hydrogen and ethene on Pd was sensitive for particle size because both di- σ bonded ethene and π -bonded ethene were redistributed.

Doyle *et al.* [56] stated that the way that hydrogen adsorbed on Pd surface is responsible for the alkene hydrogenation. They concluded that the presence of subsurface hydrogen is essential for hydrogenation to occur rather than side reactions. This conclusion was also suggested in recent publications [57] and [58]. Wood *et al.* [59] suggested that in order to obtain side reactions from alkene hydrogenation, subsurface hydrogen must be prevented.

From the findings of the previous studies and also taking into account the tendency of Pd to isomerise during alkene hydrogenation [60] it was expected that in the work reported in this thesis, isomerisation would be detected for any of the three substrates.

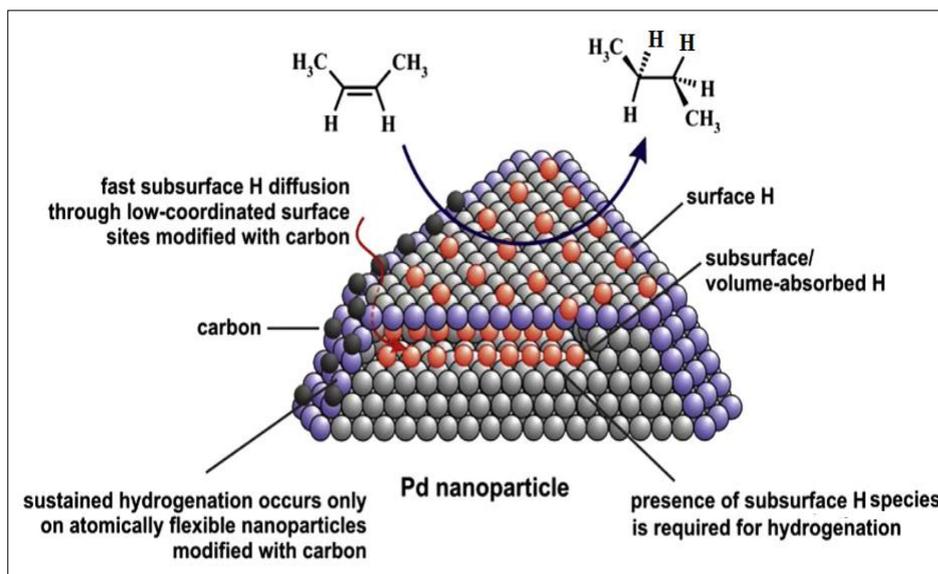


Figure 7- Proposed reaction mechanism of olefin hydrogenation on Pd nanoparticles.[61]

Lee and Zaera [62] used H-D isotopes in reactions to identify cis-trans isomerisation. They observed that cis-2-butene needed higher energy to desorb from the catalyst surface (figure 8). In other words isomerising trans-2-butene to cis-2-butene is easier than the other way around. This was attributed to stability behaviour of the isomers on Pt(111). This figure shows the elementary steps responsible for the double bond migration between 1-butene and 2-butene as well as for the cis-trans isomerisation between the 2-butenes. In general, these isomerisation reactions can be explained by a combination of rapid β -hydride eliminations from adsorbed 2-butyl to the butenes and the reverse insertions of those butenes into metal-hydrogen bonds [63].

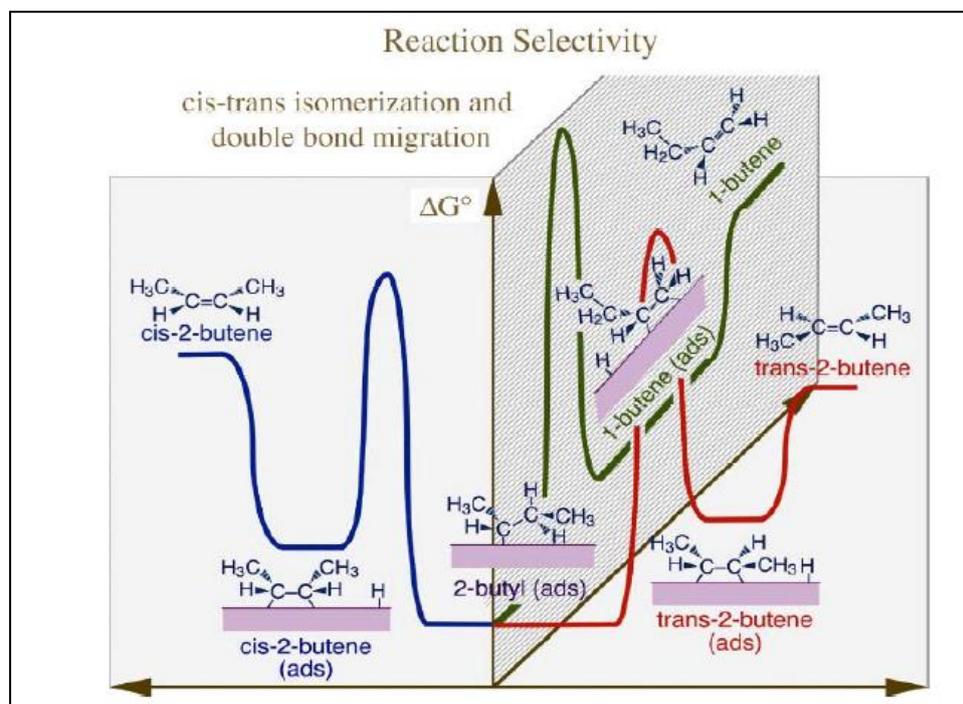


Figure 8- Schematic energy diagram for the isomerisation of butenes on Pt(111) [63].

2.2.3 Nitrile Reduction:

Von Braun *et al.* in 1923 proposed their famous mechanism for nitrile hydrogenation. They found that amines are consecutively formed from the hydrogenation of nitriles after the formation of imine as an intermediate [64]. Hence nitriles are hydrogenated to form imines before forming the primary amine. Secondary amines are formed from 1-aminodialkylamine which is an intermediate formed via the reaction between the primary amine and the imine as shown on figure 9 [65].

In cases when nitriles contain additional reducible groups such as C=C, the products of the hydrogenation reaction vary according to the group that has been hydrogenated. In the case of hydrogenating C=C the products are mainly saturated nitriles (thermodynamically more favourable [66]), when C≡N is the group that has been hydrogenated unsaturated amines are obtained and saturated amines are obtained in the case of both groups are hydrogenated [36]. This variation is highly affected by the position of the C=C double bond relative to the C≡N [36] [35].

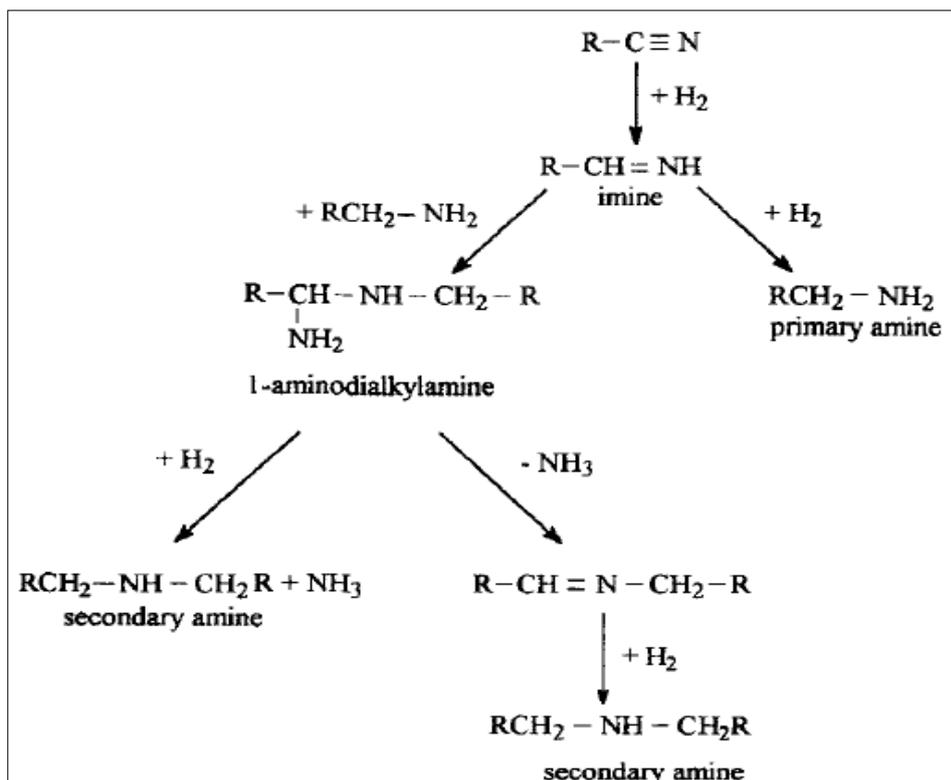
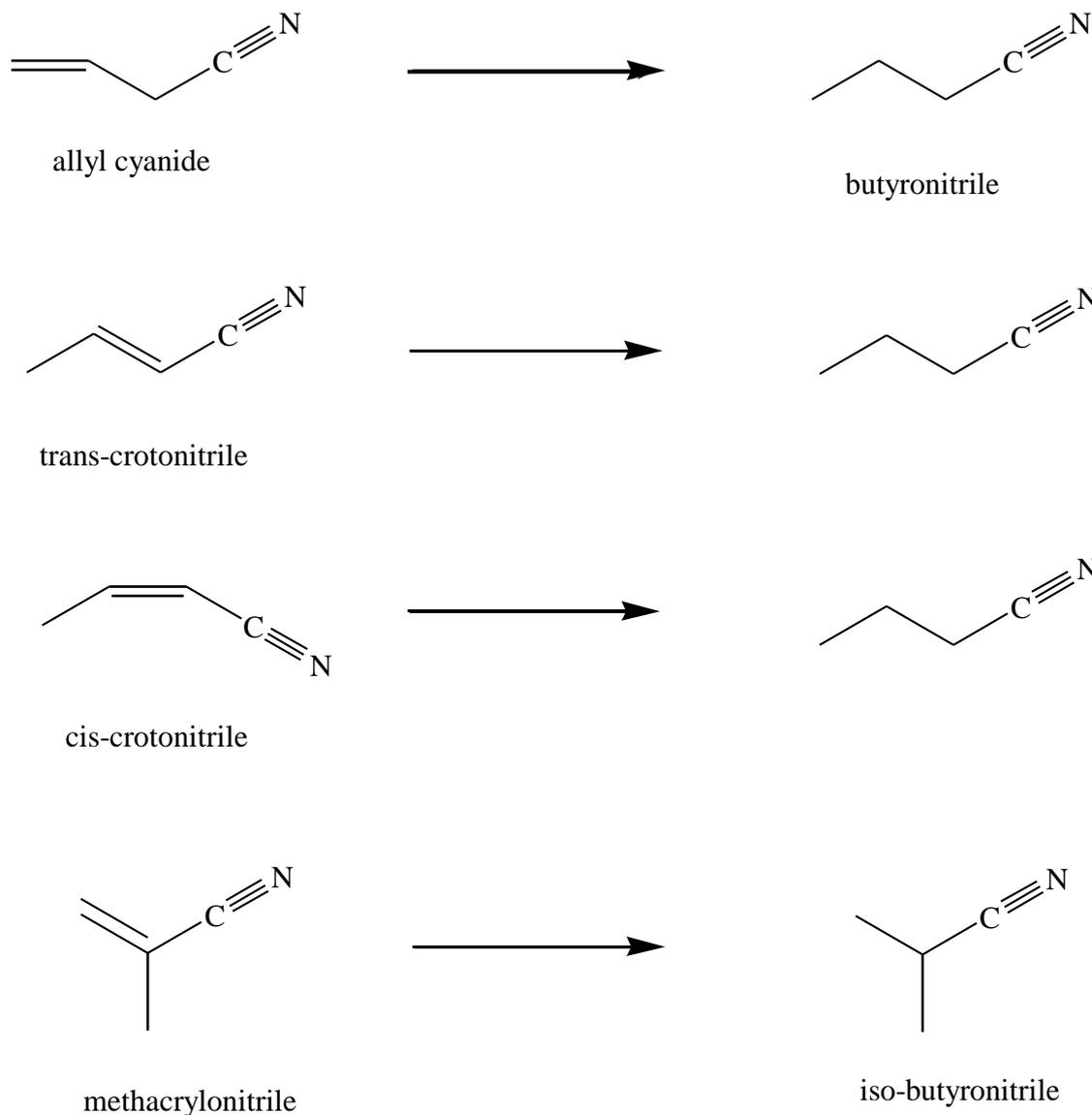


Figure 9- A scheme for Von Braun mechanism for nitrile hydrogenation [65]

- The double bond is not hydrogenated when it is sterically hindered or if it is too far from the nitrile group.
- In conjugated systems the activated double bond is hydrogenated before the nitrile.
- An additional methyl substituent at the double bond enhances the selectivity for unsaturated amines.
- The highest selectivity for unsaturated amines were reached during the hydrogenation of non conjugated systems [36].

3. Aims of project.

The aim of this project was to investigate the hydrogenation of C-4 nitriles over a Pd/alumina catalyst. The nitriles were allyl cyanide, crotonitrile, and methacrylonitrile. This combination allowed the comparison of both electronic and steric effects to be examined.



The study examined the kinetic parameters of activation energy and orders of reaction, through variation of temperature and partial pressure, as well as solvents effects and competitive hydrogenation.

4. Experimental:

All the techniques, preparations, instruments, tests, analysis and chemicals concerning this work are presented in this section.

4.1 Catalyst Preparation:

A 1% wt/wt Pd over θ -Al₂O₃ (surface area 105.6 m².g⁻¹) catalyst was prepared by impregnation. To produce 100 g of catalyst 2.5 g of Pd(NO₃)₂.2H₂O was added to 42 ml distilled water and put in ultrasonic bath to aid dispersion and mixing. The volume of water was calculated using the pore volume for the support which was 0.42 ml .g⁻¹. Subsequently the solution was put to a spray gun (DESAGA SG1) and sprayed over 100 g of support which was in a tumbling bed (Pascal lap mixer). The catalyst was dried in a drying oven at 110°C overnight. Finally, the catalyst was calcined at 500°C for 4 hours. Analysis of the metal content of the catalyst was performed by Johnson Matthey plc and was found to be 0.44 % w/w Pd.

4.2 Catalyst Characterization:

The catalyst was characterised before calcination by Thermo-Gravimetric analysis (TGA) in order to find the appropriate calcination temperature. After calcination, the surface area of the catalyst was determined by Brunauer-Emmett-Teller method (BET).

4.2.1 Thermo-Gravimetric Analysis (TGA)

TGA analysis was carried out on the catalyst before it was calcined using a combined TGA/DSC SDT Q600 thermal analyser attached to an ESS Mass Spectrometer. The analysis was conducted under a flow of 2 % O₂/Ar (100 ml.min⁻¹). The temperature was raised to 1000°C at 10°C per minute.

4.2.2 Surface area determination:

The surface area of the calcined catalyst was measured by using the Brunauer-Emmett-Teller (BET) method. Chorkendorff, I. and J.W. Niemantsverdriet [67] pointed to the principle of measuring the surface area as " physisorb an inert gas such as argon or

nitrogen and determine how many molecules are needed to form a complete monolayer". In this analysis N₂ was used as it occupies 0.162 nm² at 77 K [68].

Micromeritics Gemini III 2375 Surface Area Analyser was used as to estimate the surface area. The catalyst (0.025g) was loaded into the analyser and degassed at 110°C for 1h and purged under a flow of N₂ (30 ml.min⁻¹).

To find surface area via BET method the following formula is used:

$$P/[V(P_o-P)] = 1/V_m C + [(C-1)P]/V_m C P_o \quad [8]$$

P = Equilibrium pressure of adsorbate gas

P_o = Saturated pressure of adsorbate gas

V = Volume of adsorbed gas

V_m = Volume of monolayer adsorbed gas

C = BET Constant

$$C = e^{(q_1 - q_L)/RT} \quad [8]$$

q₁ = Heat of adsorption on the first layer

q_L = Heat of liquefaction on second and higher layers

R = Gas constant

A plot of P/[V(P_o-P)] against P/P_o should give a straight line where

$$\text{Slope (S)} = C-1/V_m C$$

$$\text{Intercept (I)} = 1/V_m C$$

V_m can be calculated according to

$$V_m = 1/(S + I) \quad [8]$$

The surface area can be calculated using the following formula

$$S_t = V_m N/M_v$$

Where M_v is the molar volume of adsorbed gas

N = Avogadro's number = 6.022 x 10²³

S_t = cross-sectional area of the adsorbed gas

4.3 Catalyst Testing:

Several parameters were common in all reactions: catalyst weight was 0.05g and solvent volume was 330 ml (of which 10 ml was separately degassed before each reaction).

4.3.1 Kinetic studies using IPA and 1-propanol as solvents.

Eleven reactions were completed for each of the three reactants using IPA as a solvent to determine activation energies (E_A) and order of reactions.

Reaction parameters were as follow:

- Reaction temperature 30, 40, 50, 60 and 70 °C, while hydrogen pressure was held at 3 barg and reactant volume was 1 ml.
- Hydrogen pressure 2, 3, 4 and 5 barg, while temperature was held at 50 °C and reactant volume was 1 ml.
- Reactant volume 0.6, 0.8, 1 and 1.2 ml, while hydrogen pressure was held at 3 barg and reaction temperature was 50 °C.

Using 1-propanol as a solvent four reactions were completed for each of the three reactants.

- Reactant volume 0.6, 0.8, 1 and 1.2 ml, while hydrogen pressure was held at 3 barg and reaction temperature was 50 °C.

4.3.2 Solvent studies using acetone, isopropylalcohol, 1-propanol, methanol, ethanol and dodecane.

For each solvent, three reactions were completed for each of the three reactants.

The reaction conditions were as follows:

- Reaction temperature was 40°C.
- H₂ pressure was 3 barg.

4.3.3 Mixture of reactants to investigate competitive hydrogenation.

The reactants were hydrogenated together using IPA as a solvent as the following sequence:

allylcyanide + methacrylonitrile

allylcyanide + crotonitrile

methacrylonitrile + crotonitrile

allylcyanide + methacrylonitrile + crotonitrile

The reaction conditions were as follows:

- Reaction temperature was 50°C.
- H₂ pressure was 3 barg
- Reactant volume was 1ml for each reactant.

4.4 Instruments:

The instruments, used for the hydrogenation reactions and the analysis, were:

4.4.1 Stirred Tank Reactor:

The liquid-phase hydrogenation reactions were executed in a Buchi laboratory autoclave (figure 10) fitted with a hydrogen on demand system.

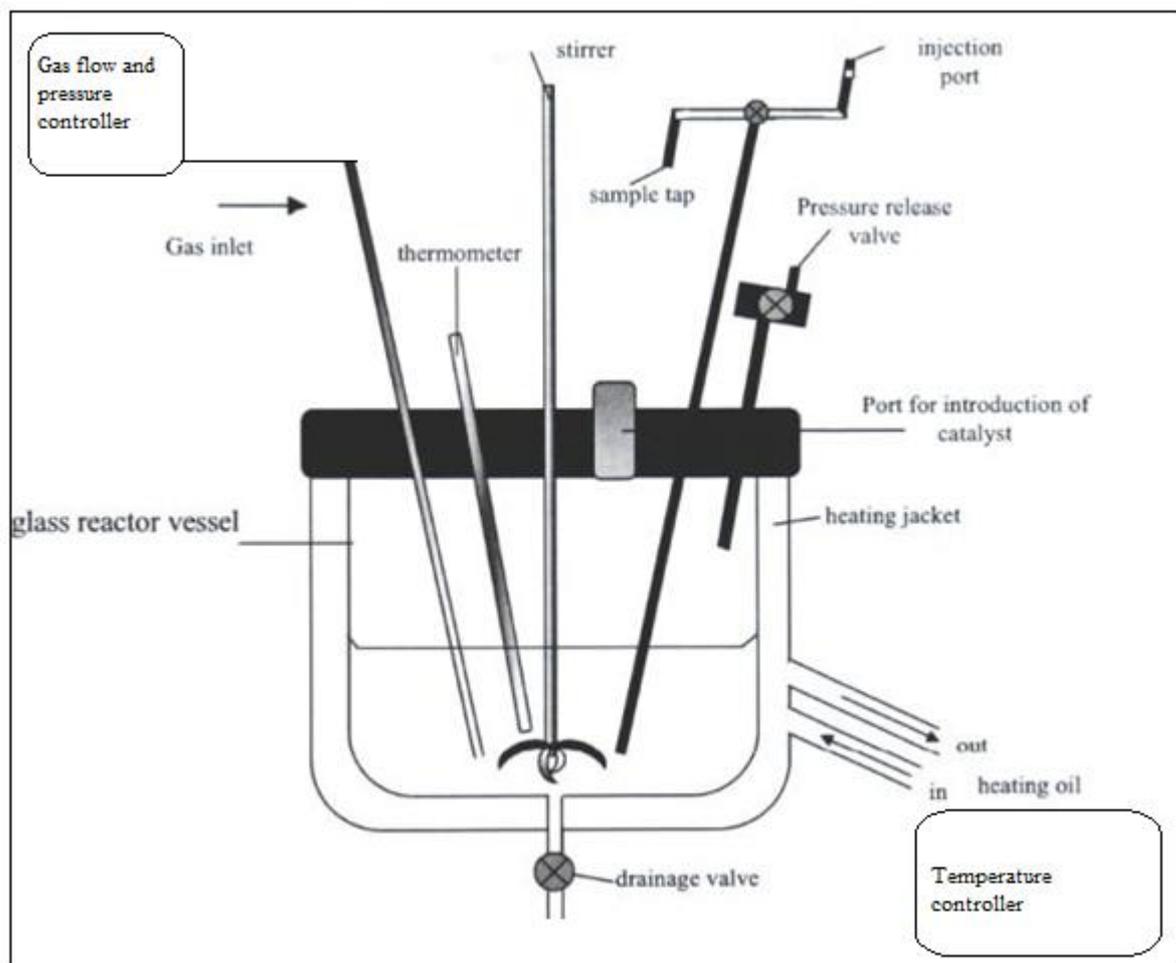


Figure 10- Stirred Tank Reactor

It is a glass-metal cylindrical vessel with bottom opening equipped with:

- a Buchi 300 mechanical stirrer with a rate that could be varied between 0-2400 rpm.
- Refrigerated and heating circulating system (Julabo) which passes heated oil around the vessel. A 100 Pt thermocouple is connected to the heating system.

- Buchi gas control (Pressflow gas controller .bpc. 1202) which is used to control the gas pressure and flow to the reactor.

4.4.2 Gas chromatography (GC):

All samples were analyzed via a Focus GC (figure 11). The column installed in the GC was an HP 1701, 30 meters long and 0.025 diameter.

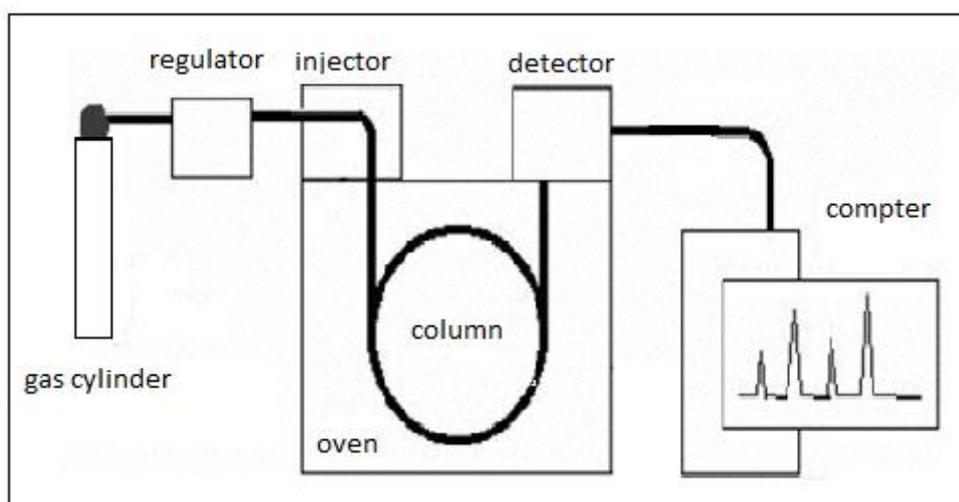


Figure 11- Gas Chromatography.

1 μ l of each sample was injected to the GC and it was detected by an FID detector (flame ionization detector) which is used to detect compounds that contain C in their formula.

The GC column heating profile is shown in figure 12.

- **GC conditions were as follow:**

Injector temperature: 230°C

Carrier gas: Helium

Detector temperature: 300°C

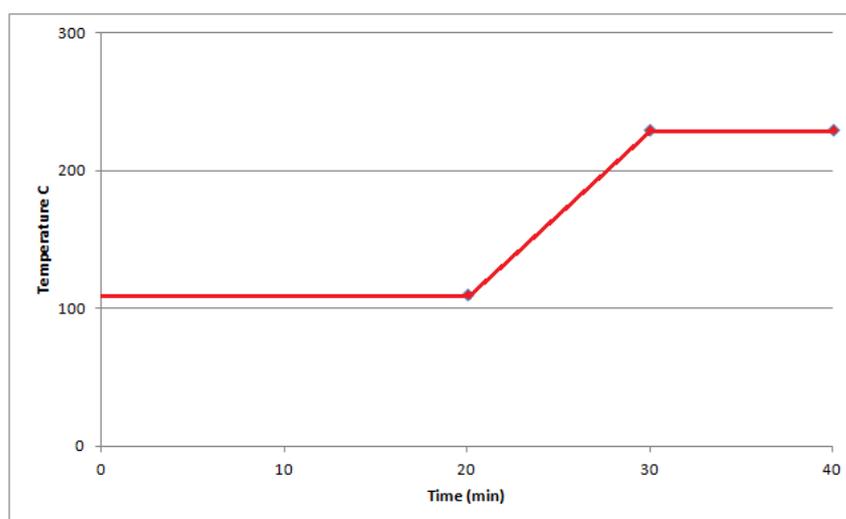


Figure 12- GC column heating profile

4.4.2.1 GC Calibration:

Before reactions, all reactants and expected products were prepared in different concentrations (10, 30, 50, 70 and 100 %) then injected into the GC. Peak areas resulting from GC analysis were plotted against concentrations and the gradients of the lines were used to generate conversion factors to allow concentrations to be determined from peak areas of reactor eluants. Figure 13 shows the gradients for all substances used in the reactions.

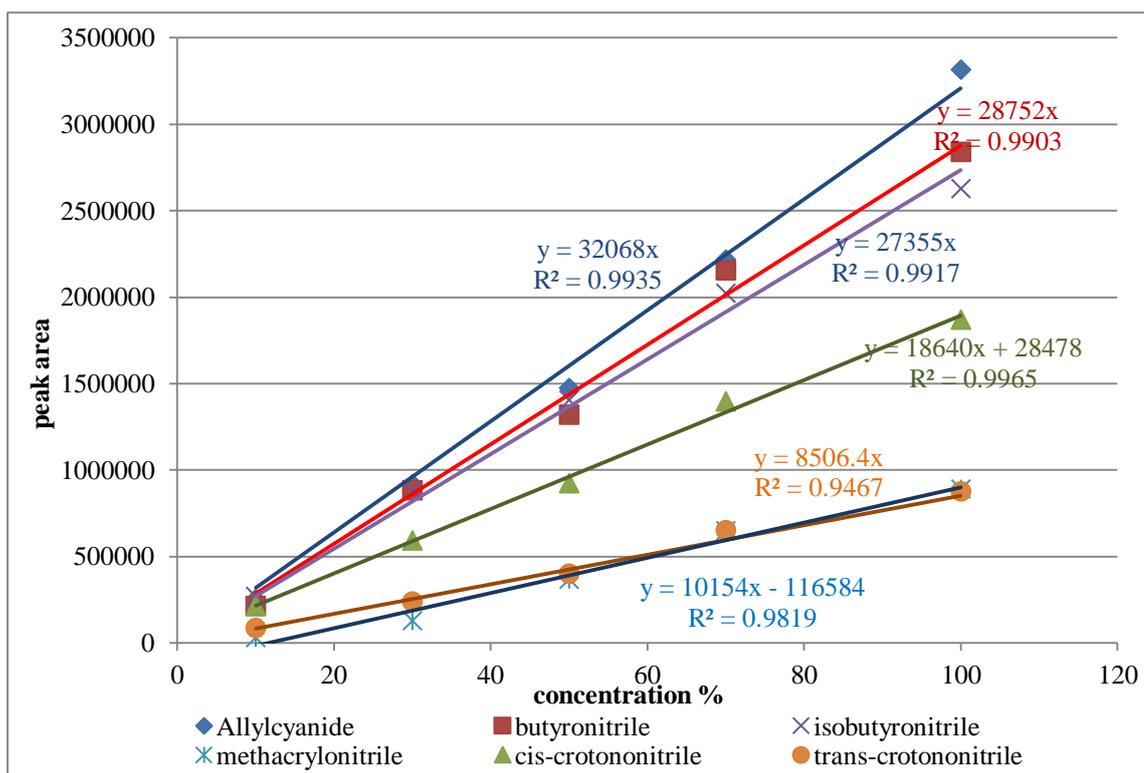


Figure 13- Calibrations for reactants and products.

4.5 Pre-reaction procedure:

The three reactants (allylcyanide, crotonitrile and methacrylonitrile) were hydrogenated with same procedure where the catalyst was reduced before each reaction. The amount of reactant used, unless otherwise specified, was 1ml (allylcyanide = 0.0126 mole, methacrylonitrile = 0.0119 mole and crotonitrile = 0.0124 mole)

4.6 Catalyst Reduction:

The catalyst was reduced ($\text{PdO} + \text{H}_2 \rightarrow \text{Pd} + \text{H}_2\text{O}$) before all reactions to achieve the metallic state where it becomes active for hydrogenation reactions. The reduction process was carried out by introducing 0.05 g of the catalyst with 320 ml of solvent into the

reaction vessel from the catalyst port on the top of the vessel. After closing the system tightly, the mechanical stirrer was set to 300 rpm to mix the catalyst with the solvent. After that the system was heated to 70 °C. Then hydrogen was pumped through the reaction vessel after opening the pressure valve. The flow was set to 100 ml.min⁻¹ and 0.5 barg. After 30 minutes the hydrogen flow was stopped, pressure valve closed and the mechanical stirrer was set to zero.

4.7 Executing hydrogenation reaction:

After the completion of catalyst reduction, the system was adjusted to the desired temperature. The pressure was set to the desired amount from the gas control unit. Once the temperature stabilized the reactant and 10 ml of degassed solvent were injected into the reactor through the injection port. The reactant was injected first, followed by the solvent to wash any remaining reactant in the reactor. The system was then mechanically stirred at 1000 rpm and hydrogen introduced to the reactor to reach the required pressure. Timing also started at the same time the gas was introduced to the reactor and the first sample was collected using the sampling tap after reducing the stirrer speed to zero. The stirrer was set to 1000 rpm after collecting the sample. After five minutes the stirrer was set to zero again and the second sample was collected using the sampling tap after opening it for few seconds to remove pressure and any previous residue in the sampling tube.

Eighteen samples were taken for every reaction as follows: for the first 30 minutes a sample was collected every 5 minutes. After that a sample was taken every 10 minutes for the next 60 minutes and finally, for the following 90 minutes a sample was taken every 15 minutes. Samples were analyzed by the gas chromatography.

After collecting the last sample, the heater was turned off, the gas controller was stopped and the mechanical stirrer was reduced to 300 rpm. The pressure valve was opened to release pressure from the reactor and the catalyst port was unlocked. After that the content of the reactor was drained from the bottom of the reaction vessel via the drainage valve. Then the drainage valve was closed and a solvent (IPA or acetone) was introduced to the vessel via catalyst port for cleaning. The port was tightly closed and the stirrer was set to 1000 rpm for 30 seconds before being reduced to 300 rpm. Finally the remaining solvent was drained as before into a waste drum. The same procedure was performed for all reactions.

4.8 Chemicals:

All chemicals used are listed in table 2 were used directly without any further purification.

Table 2- Chemicals

Substance	Producer	Purity
Hydrogen	BOC	99%
Pd(NO ₂) ₃	Alfa Aesar	98%
Allylcyanide	Sigma	98%
Butyronitrile	Sigma	98 %
Crotonitrile (cis-trans)	Sigma	99 %
Methacrylonitrile	Sigma	99 %
Isobutyronitrile	Sigma	99.60%
Acetone HPLC	Fisher	99.98%
1-propanol	Alfa Aesar	99+ %
Isopropyl alcohol	Sigma	99.50%
Methanol HPLC	Fisher	99.90%
Ethanol	VWR	99.90%

5. Results:

5.1 Catalyst Characterisation:

5.1.1 Surface area:

The surface area of the catalyst was determined via a BET isotherm as explained in section 2.3.2. Results showed that the surface area of the catalyst after calcination was $250 \text{ m}^2 \text{ g}^{-1}$.

5.1.2 TGA:

In order to determine the appropriate calcination temperature to be applied, the decomposition of the catalyst precursor was examined by TGA in 2% O_2/Ar . In figure 14 it can be seen that there is a general weight loss between 50 – 450 °C. From mass spectrometry the weight loss can be associated with the loss of water, NO and NO_2 from the sample. Therefore the temperature chosen for calcination was 500 °C.

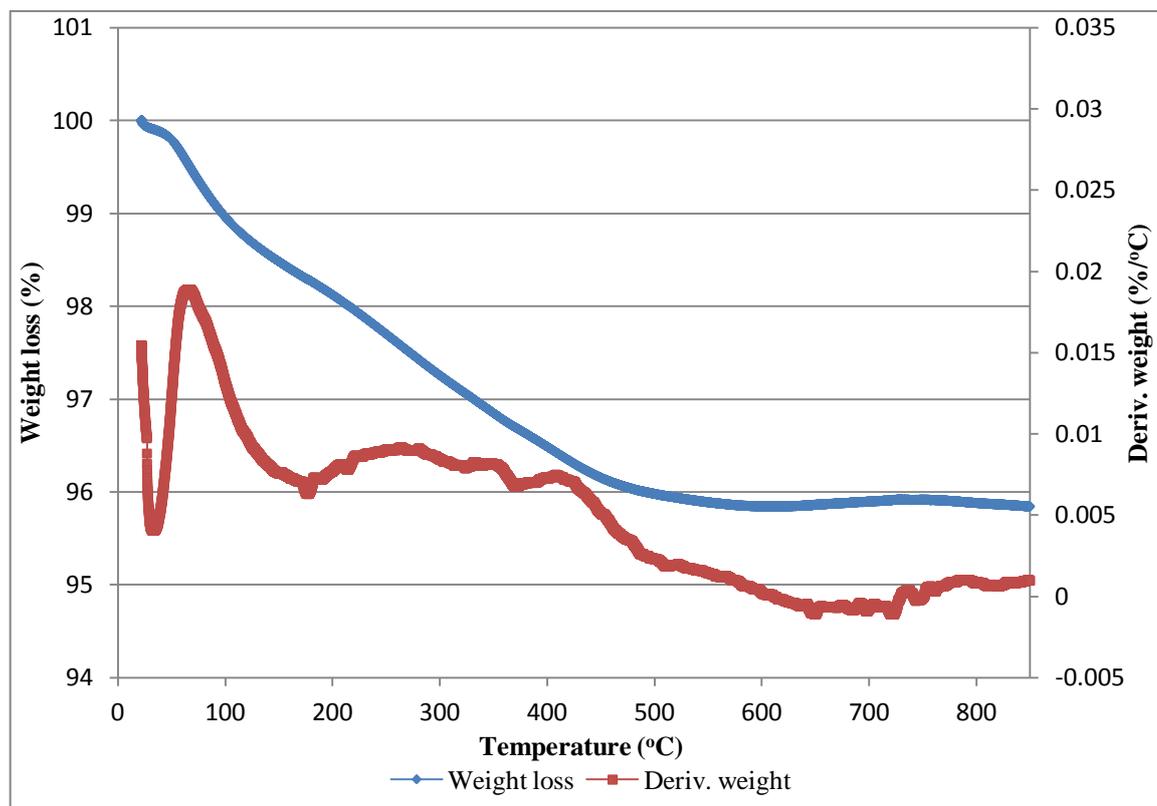
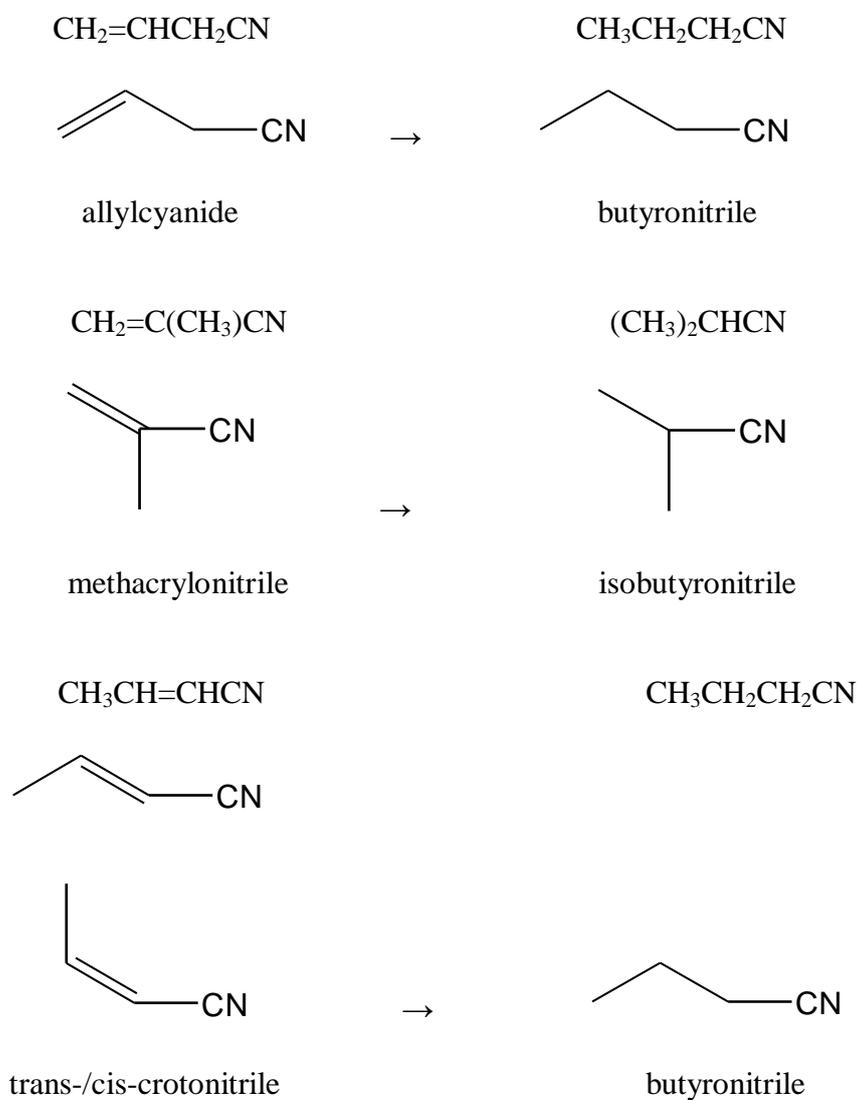


Figure 14- TGA profile for the catalyst before calcinations.

5.2 Catalyst Testing:

The results obtained from the GC show that the products from all of the liquid phase hydrogenations were the corresponding saturated nitriles, no saturated amines or unsaturated amines were detected.



5.2.1 Kinetic studies:

This section reports the results from the hydrogenation of the three reactants using IPA as a solvent to determine the kinetic parameters. In addition, it involves the comparison of the kinetics observed when 1-propanol is used as the solvent rather than IPA.

5.2.1.1 Temperature Variation:

Each reactant (1 ml) was hydrogenated using IPA as a solvent under 3 barg H₂ and the temperature was varied (30, 40, 50, 60, and 70 °C). The results obtained from temperature variation were used to calculate activation energy. Figures 15 and 16 show reaction profiles at two different temperatures. As expected both show an increasing product formation and decreasing reactant concentration.

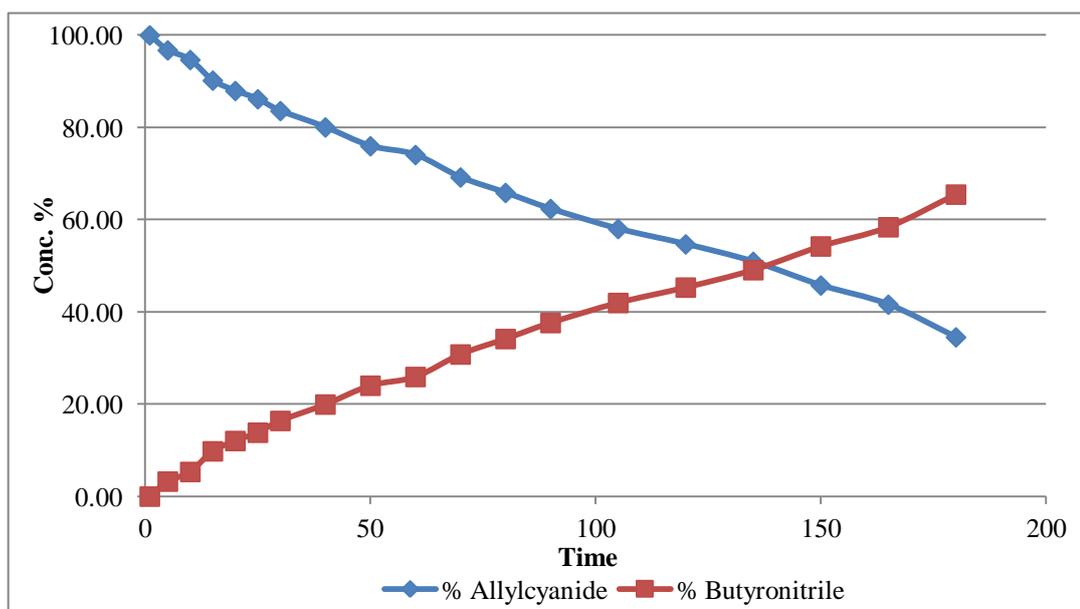


Figure 15- Allylcyanide hydrogenation profile at 30 °C

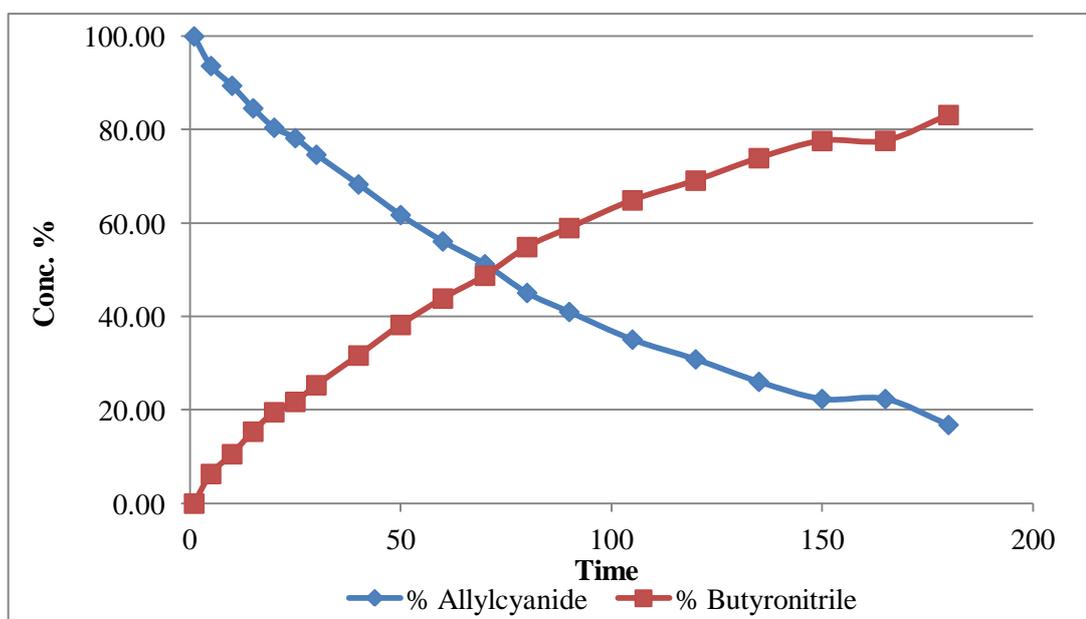


Figure 16- Allylcyanide hydrogenation profile at 60 °C

- **Determination of the rate constant (k):**

The data from each reaction was plotted against $\ln([A]_o / [A]_t) = k.t$, which is the integrated form of the rate expression for a first order reaction [69], where;

$[A]_o$ and $[A]_t$ are concentration of substrate in mole.l^{-1} at time 0 and time t.

t is time in minutes

k is the rate constant in min^{-1}

plotting $\ln([A]_o / [A]_t)$ against time (t) will give a linear equation where the slope = k.

In tables 3-5 conversion after 180 minutes is reported for the three reactants as well as the time taken to reach 20% conversion of each substrate. The first order rate constant of each reaction is also reported.

Table 3- Allylcyanide conversion at various temperatures under 3 barg H_2

Temp. °C	30	40	50	60	70
Con. after 180 min. %	65	80	87	83	60
Time to 20 % conv. (min)	40	30	20	20	30
rate constant. k (min^{-1})	0.0057	0.0079	0.0094	0.0097	see text

As expected the conversion of allylcyanide (Table 3) after 180 min. increased from 65 % to 87 % with increasing temperature. However there was a decrease in conversion to 60 % at 70 °C. On examination of the first order rate constant plot from the 70 °C experiment it was seen that the fit was less good than those between 30-60 °C (Figure 17 shows an example of a first order plot). Indeed plotting the data at 70 °C to a second order rate equation $kt = ([A]_o - [A]_t) / ([A]_o [A]_t)$ provided a better fit (Figures 18 and 19).

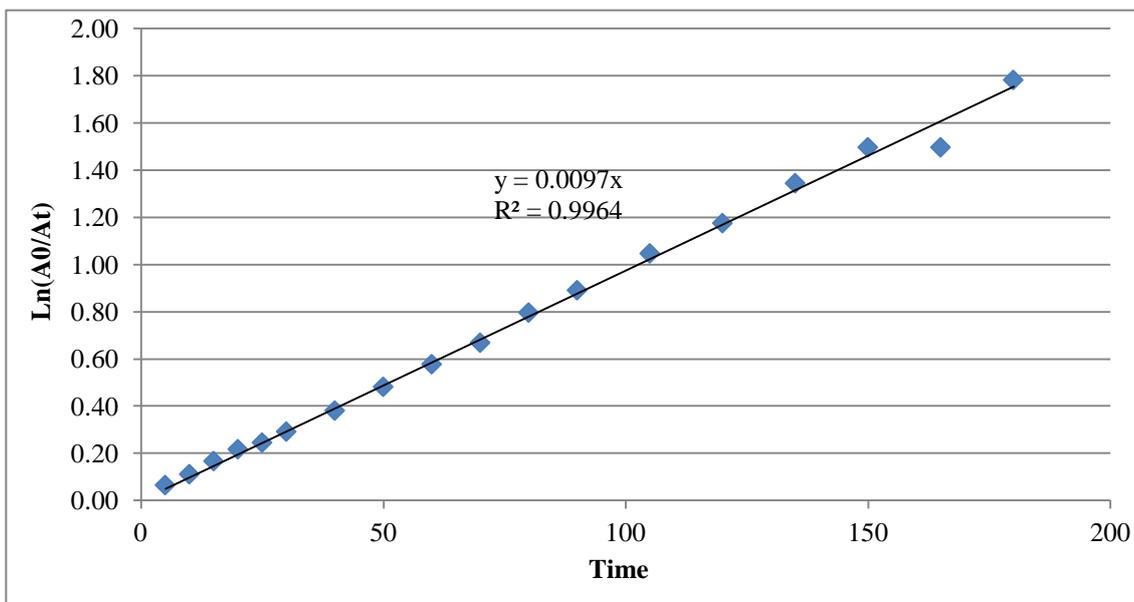


Figure 17- First order rate constant for allylcyanide at 60 °C

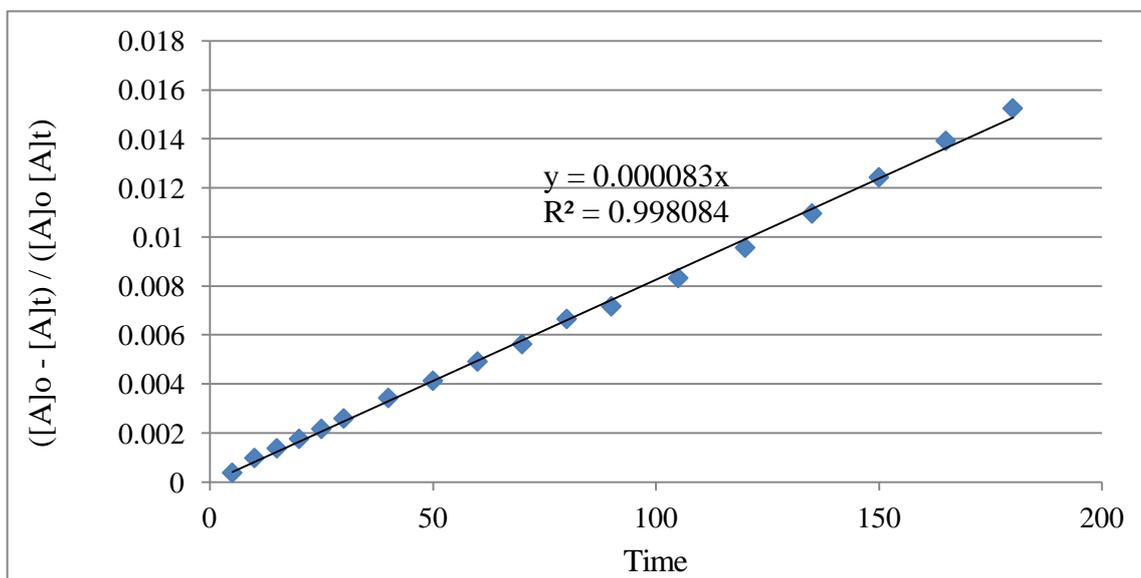


Figure 18- Second order rate constant for allylcyanide at 70 °C

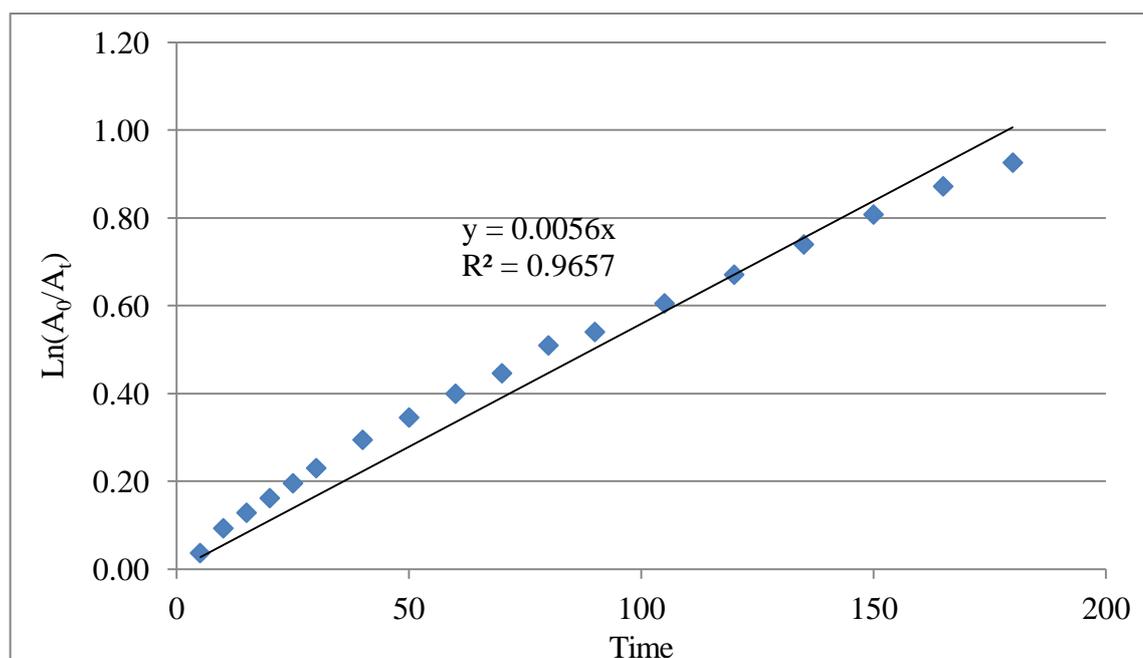


Figure 19- First order rate constant for allylcyanide at 70 °C

Table 4- Crotonitrile conversion with different temperatures under 3 barg H₂

Temp. °C	30	40	50	60	70	
Con. after 180 min %	62	76	91	87	78	
Time to 20 % conv. (min)	40	30	15	10	15	
rate constant. k (min ⁻¹)	cis	0.0056	0.0073	0.0177	0.0166	0.0135
	trans	0.0058	0.0087	0.0158	0.0138	0.0098

Table 5- Methacrylonitrile conversion with different temperatures under 3 barg H₂

Temp. °C	30	40	50	60	70
Con. after 180 min %	55	83	85	76	77
Time to 20 % conv. (min)	50	20	15	15	15
rate constant. k (min ⁻¹)	0.0049	0.0122	0.0166	0.0142	0.0101

- Activation Energy (E_A) Determination:

Activation energy is known as the minimum amount of energy required to start a reaction. It is measured in kJ.moles⁻¹. When the activation energy is high the reaction rate is very sensitive to temperature [70].

The activation energy was determined using the Arrhenius equation which is an equation that represents the dependence of the rate constant k of a reaction on the absolute temperature T:

$$k = A.\exp(-E_a/RT) \text{ [69]}$$

where, k is rate constant, A is the pre-exponential factor, E_a is the activation energy, R is the gas constant ($8.314 \text{ J.K.mol}^{-1}$) and T is the temperature in Kelvin ($0^\circ\text{C} = 273 \text{ K}$). Taking the natural log gives the equation,

$$\ln(k) = (-E_A/R).(1/T) + \ln(A)$$

hence plotting $\ln(k)$ versus $1/T$ will give a linear line with the general formula:

$$y = m x + c, \text{ where } E_A = -m.R.$$

Activation energy for the allylcyanide reaction was calculated as an example.

E_A can be calculated after plotting $\ln(k)$ versus $1/T$

T	K	1/T	Ln (k)
303	0.0057	0.0033	-5.16729
313	0.0079	0.003195	-4.84089
323	0.0094	0.003096	-4.66705

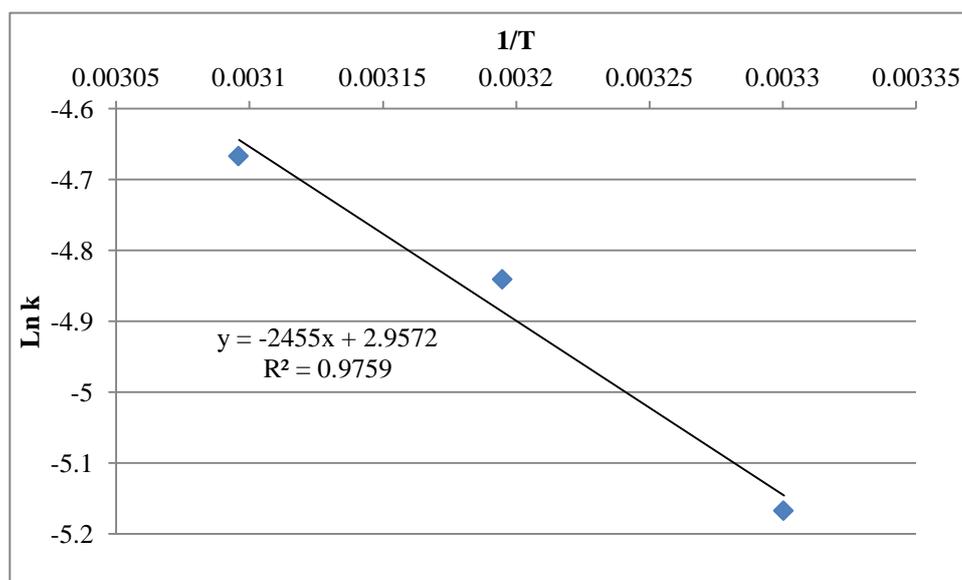


Figure 20- Allylcyanide activation energy plot.

$$k = A \exp (-E_A /RT)$$

$$\ln(k) = (-E_A/R).(1/T) + \ln(A)$$

$$y = m x + c$$

$$E_A = -m.R$$

$$y = -2455 + 6.0462$$

$$E_A = - (-2455 * 8.314)/1000$$

$$E_A = 20.4 \text{ kJ.mol}^{-1}$$

The activation energies for the hydrogenation reactions of the three reactants were determined as above and are reported in table 6.

Table 6- Activation energies calculated for each of the reactions.

Reactant	Allylcyanide	Methacrylonitrile	Crotonitrile	
			Cis	trans
Activation Energy [kJ.mol ⁻¹]	20	50	46	40

- Determining the order of reaction:

Order of reactions are used to classify reactions according to their kinetics. They are obtained from experimental data [70]. They indicate the relation between concentration or pressure with the rate of reaction.

Order of reaction determination depending on concentration: $r = k [A]^x [H_2]^y$ $\ln r = \ln k + x \ln [A] + y \ln [H_2]$ plotting $\ln r$ versus $\ln [A]$ will give a straight line with the form $y = m x + c$ where m is order of reaction

1- Order of reaction determination depending on H₂ pressure:

$$\ln r = \ln k + x \ln [A] + y \ln [H_2]$$

plotting $\ln r$ versus $\ln [H_2]$ will give a straight line with the form

$$y = m x + c \quad \text{where } m \text{ is order of reaction}$$

5.2.1.2 Order of reaction in hydrogen (pressure variation).

Each reactant was hydrogenated, with IPA as a solvent, at 50 °C, using hydrogen pressures of 2, 3, 4 and 5 barg. The results obtained from the pressure variation are reported in tables 7-9 and were used to determine reaction order.

Table 7- Allylcyanide conversion with different pressures at 50°C

Pressure. barg	2	3	4	5
Con. after 180 min %	78	87	84	89
Rate (μmol.l ⁻¹ .min ⁻¹)	8	13	16	22
rate constant. k (min ⁻¹)	0.0075	0.0094	0.0086	0.0103

Table 8- Crotonitrile conversion with different pressures at 50°C

Pressure. barg	2	3	4	5	
Con. after 180 min %	61	91	59	87	
Rate ($\mu\text{mol.l}^{-1}.\text{min}^{-1}$)	11	23	15	34	
rate constant. k (min^{-1})	cis	0.006	0.0177	0.0068	0.0164
	trans	0.0064	0.0158	0.006	0.0134

Table 9- Methacrylonitrile conversion with different pressures at 50°C

Pressure. barg	2	3	4	5
Con. after 180 min %	83	85	86	88
Rate ($\mu\text{mol.l}^{-1}.\text{min}^{-1}$)	20	24	30	24
rate constant. k (min^{-1})	0.0139	0.0166	0.022	0.0204

The order of reaction was calculated for the three reactants and as an example the reaction order in hydrogen for allylcyanide hydrogenation is shown in detail in figure 21:

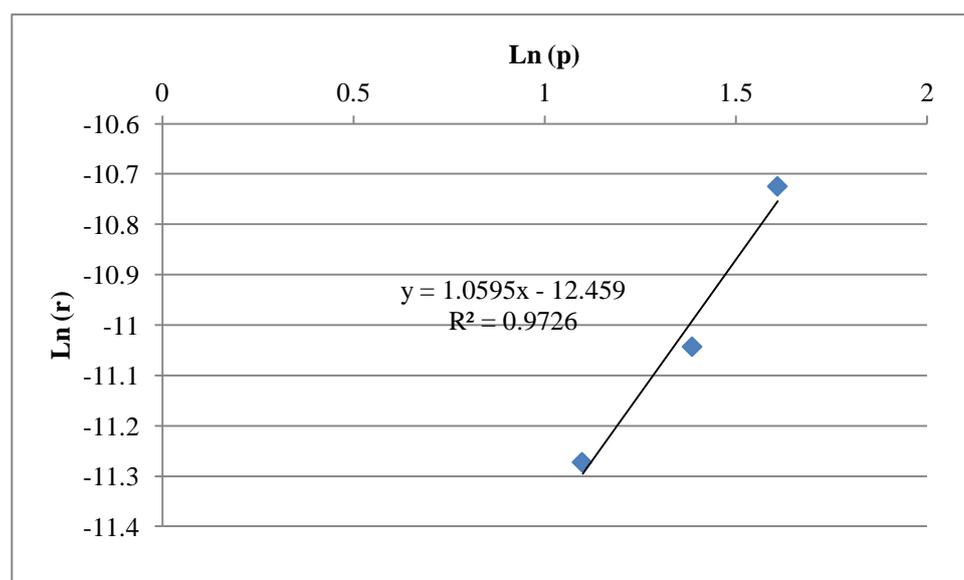


Figure 21- Reaction order of Hydrogen depending pressure for allylcyanide

From figure 21 the gradient of line is ~1 therefore the order of reaction fits first order in this range. The reaction order for the other reactions was calculated in the same method and is shown in table 10.

Table 10- Order of reaction in hydrogen

Reactant	Allylcyanide	Methacrylonitrile	Crotonitrile
Order of reaction	1	0.5	1

5.2.1.3 Order of reaction in organic (variation of concentration).

Each reactant was hydrogenated using IPA as a solvent under 3 barg H₂ at 50 °C where the volume of organic reactant was varied from 0.6 ml to 1.2 ml. The results obtained from varying the organic concentration, shown in tables 11-13, were used to determine the reaction order.

Table 11- Allylcyanide conversion with different volumes under 3 barg H₂ at 50°C

Reactant volume (ml)	0.6	0.8	1.0	1.2
Con. after 180 min %	100	85	87	81
Rate ($\mu\text{mol.l}^{-1}.\text{min}^{-1}$)	17	19	13	14
rate constant. k (min^{-1})	0.0126	0.01	0.0093	0.0078

Table 12- Crotonitrile conversion with different volumes under 3 barg H₂ at 50°C

Reactant volume (ml)	0.6	0.8	1.0	1.2	
Con. after 180 min %	92	94	91	91	
Rate ($\mu\text{mol.l}^{-1}.\text{min}^{-1}$)	18	21	23	36	
rate constant. k (min^{-1})	cis	0.0194	0.0205	0.0177	0.0188
	trans	0.0158	0.0204	0.0158	0.0192

Table 13- Methacrylonitrile conversion with different volumes under 3 barg H₂ at 50 °C

Reactant volume (ml)	0.6	0.8	1.0	1.2
Con. after 180 min %	87	84	85	61
Rate ($\mu\text{mol.l}^{-1}.\text{min}^{-1}$)	22	18	24	28
rate constant. k (min^{-1})	0.0192	0.0154	0.0166	0.0122

- Order of reaction determination depending on concentration:

The order of reaction was calculated for the three reactants depending on concentration variation and as an example the reaction order in organic for allylcyanide hydrogenation is shown in detail figure 22.

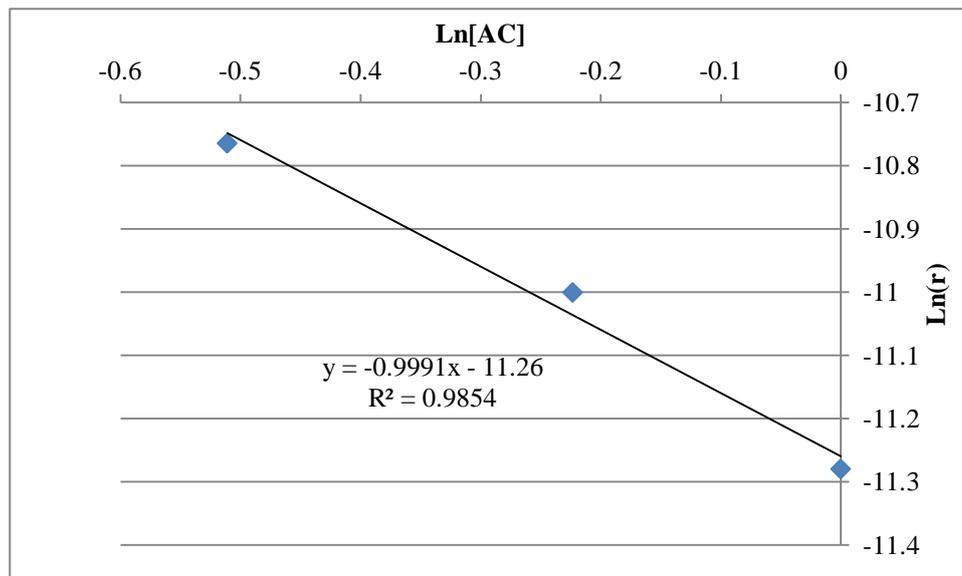


Figure 22- the reaction order of allyl cyanide depending on concentration

From figure 22 the gradient of line is -1 therefore the order of reaction in allyl cyanide fits negative first order.

The reaction orders for the other reactions were calculated in the same method and are shown in table 14.

Table 14- Order of reactions depending on concentration.

Reactant	Allyl cyanide	Methacrylonitrile	Crotonitrile
Order of reaction	-1	1	0.5

- Kinetic description of the reactions:

After finding the activation energies (table 6) and reaction orders (tables 10 and 14) for the three reactants the kinetic description for each reaction can be described as the following:

$$k = A e^{(-EA/RT)}$$

$$r = k [\text{Conc.}]^x (\text{H}_2)^y \quad \text{then}$$

$$r = A e^{(-EA/RT)} \cdot [\text{AC}]^x (\text{H}_2)^y$$

$$\text{Allyl cyanide:} \quad r = A e^{(-20/RT)} \cdot [\text{A}]^{-1} (\text{H}_2)^1$$

$$\text{Methacrylonitrile:} \quad r = A e^{(-50/RT)} \cdot [\text{M}]^1 (\text{H}_2)^{0.5}$$

$$\text{Crotonitrile: cis} \quad r = A e^{(-46/RT)} \cdot [\text{C}_{\text{cis}}]^{0.5} (\text{H}_2)^1$$

$$\text{trans} \quad r = A e^{(-40/RT)} \cdot [\text{C}_{\text{trans}}]^{0.5} (\text{H}_2)^1$$

5.2.2 Order of reaction in 1-propanol.

Tables 15-17 show the comparison between IPA and 1-propanol as mediums for the hydrogenation reactions. Reaction conditions were fixed at 40 °C and 3 barg hydrogen pressure. Only the volume of substrate was varied. The order of reactions depending on concentration was calculated as explained earlier.

Table 15- Allylcyanide conversion with different concentrations of reactant after 180 min using IPA & 1-propanol

	Vol (ml) Solvent	0.6	0.8	1.0	1.2
Conv.%	IPA	100	85	87	81
	1-propanol	58	64	89	60
Rate ($\mu\text{mol.l}^{-1}.\text{min}^{-1}$)	1-propanol	34	40	47	49

In IPA, 0.6 ml of allylcyanide was completely converted to butyronitrile after 180 min, while only 58 % was converted to butyronitrile in 1-propanol. In addition, the conversion of allylcyanide in IPA is always over 80 % for the each concentration, whereas in 1-propanol, the conversion increased from 58 % to 89 % as the concentration was increased. However with the most concentrated solution (1.2 ml) only 60 % of the allylcyanide was converted to butyronitrile in 1-propanol.

Table 16- Crotonitrile conversion with different concentrations after 180 min using IPA & 1-propanol

	Vol (ml) solvent	0.6	0.8	1.0	1.2
Conv.%	IPA	92	94	91	91
	1-propanol	89	75	99	99
Rate ($\mu\text{mol.l}^{-1}.\text{min}^{-1}$)	1-propanol	7	8	12	13

Table 17- Methacrylonitrile conversion with different concentrations after 180 min using IPA & 1-propanol

	Vol (ml) solvent	0.6	0.8	1.0	1.2
Conv.%	IPA	87	84	85	61
	1-Propanol	70	81	90	73
Rate ($\mu\text{mol.l}^{-1}.\text{min}^{-1}$)	1-propanol	10	15	19	20

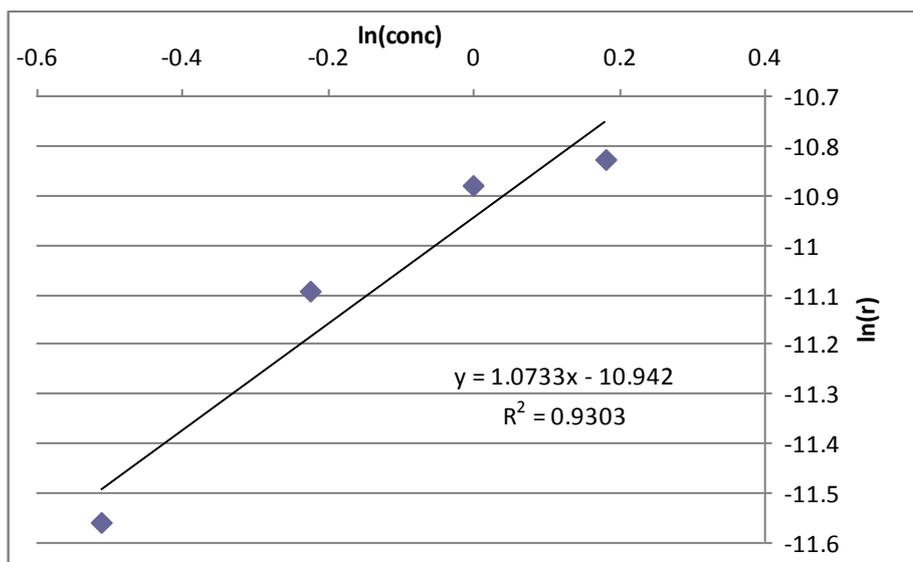


Figure 23. Reaction order of Methacrylonitrile depending on concentration using 1-propanol as a solvent.

From figure 23 the gradient of line is ~1 therefore the reaction fits the first order in this range.

The reaction orders for the other reactions were calculated in the same method and are shown in table 18.

Table 18- Order of reaction depending on concentration using 1-propanol as a solvent

Reactant	Allylcyanide	Methacrylonitrile	Crotonitrile
Order in 1-propanol	0.5	1	1
Order in IPA	-1	1	0.5

5.2.3 Liquid Phase Hydrogenation in different solvents:

All the three reactants were hydrogenated under the same conditions using different solvents. The results are shown in table 19.

Table 19- Conversion after 180 min in different solvents

Reactant	Allylcyanide	Methacrylonitrile	Crotonitrile	
Product	Butyronitrile	Isobutyronitrile	Butyronitrile	
Solvent				
Isopropylalcohol (IPA)	80 %	83 %	76 %	
k (min⁻¹)	0.0098	0.0122	Cis 0.0075	Trans 0.0055
1-Propanol	27 %	52 %	70 %	
k (min⁻¹)	0.0024	0.0057	Cis 0.0062	Trans 0.0055
Acetone	82 %	86 %	78 %	
k (min⁻¹)	0.0099	0.0121	Cis 0.0076	Trans 0.0076
Ethanol	65 %	90 %	82 %	
k (min⁻¹)	0.0084	0.0146	Cis 0.0079	Trans 0.0126
Methanol	62 %	73 %	70 %	
k (min⁻¹)	0.0089	0.0097	Cis 0.0073	Trans 0.0113
Dodecane	22 %	45 %	50 %	
k (min⁻¹)	0.0013	0.0034	Cis 0.0038	Trans 0.0046

The conversion for the three reactants was varied from solvent to another. Isopropyl alcohol and acetone gave rise to high conversions while dodecane resulted in the lowest conversion.

For example, with IPA as solvent, 80 % of allylcyanide was hydrogenated to butyronitrile after 180 minutes as shown on figure 24, while only about 20 % of the same reactant was hydrogenated after 180 minutes when dodecane was used as a solvent figure 25.

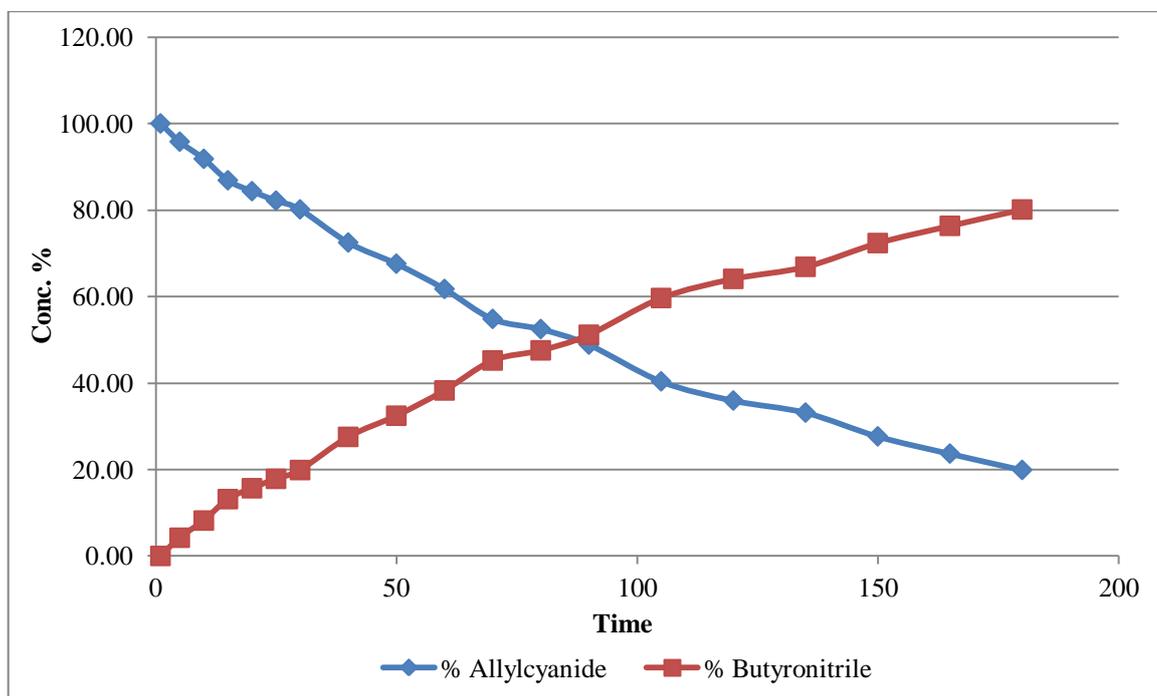


Figure 24- Allylcyanide hydrogenation using IPA.

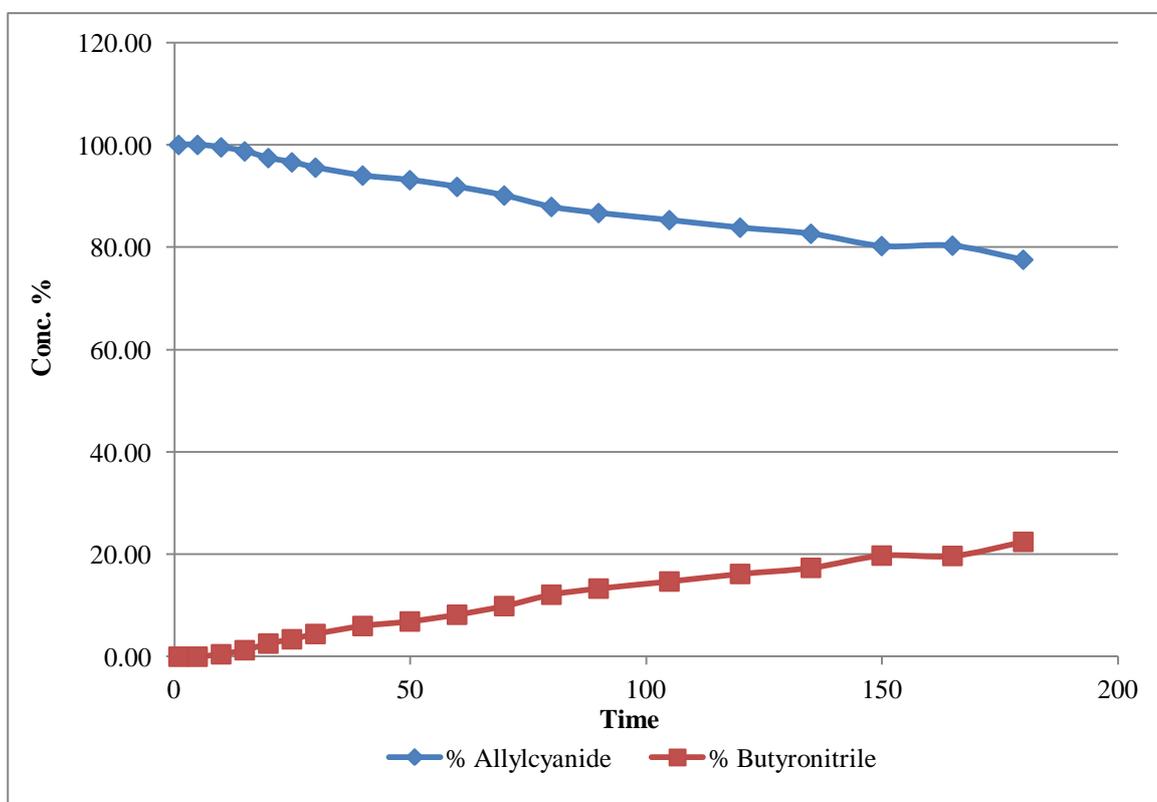


Figure 25- Allylcyanide hydrogenation using dodecane.

5.2.4 Competitive hydrogenation:

The three reactants were hydrogenated in pairs and as a mixture of all three reactants. Reaction conditions were constant for all reactions, 1 ml of each substrate at 50 °C, under 3 barg and by using IPA as a solvent. Before showing the results obtained from these mixtures, it is worth taking into consideration the way they react separately under the same conditions (figure 26). It can be seen that the reactivity of the three isomers is very similar.

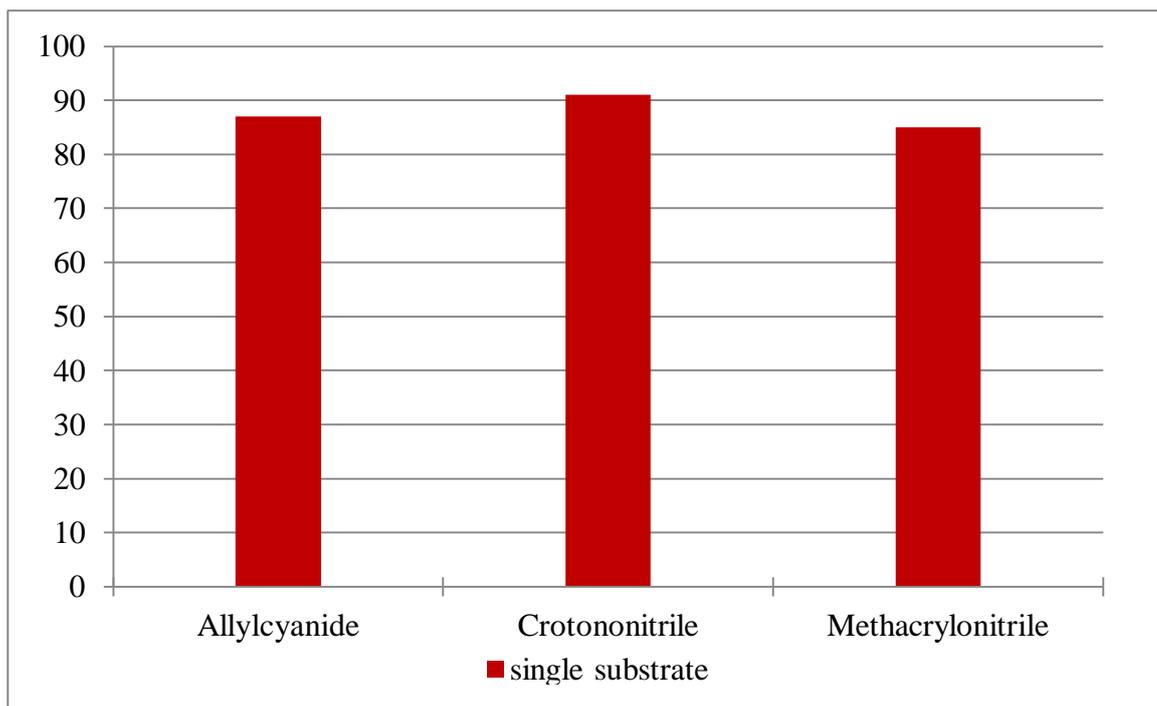


Figure 26- Hydrogenation of the three substrates separately

The results are summarised in figure 26. Table 20 shows the conversions of each substrate as single and as a mixture.

Table 20- Conversions for substrates in single and mixture form after 180 min reaction

	As	Cs	Ms
As	87	-	-
Cs	-	91	-
Ms	-	-	85
A+C	91	65	-
C+M	-	73	75
A+M	68	-	41
A+C+M	86	65	46

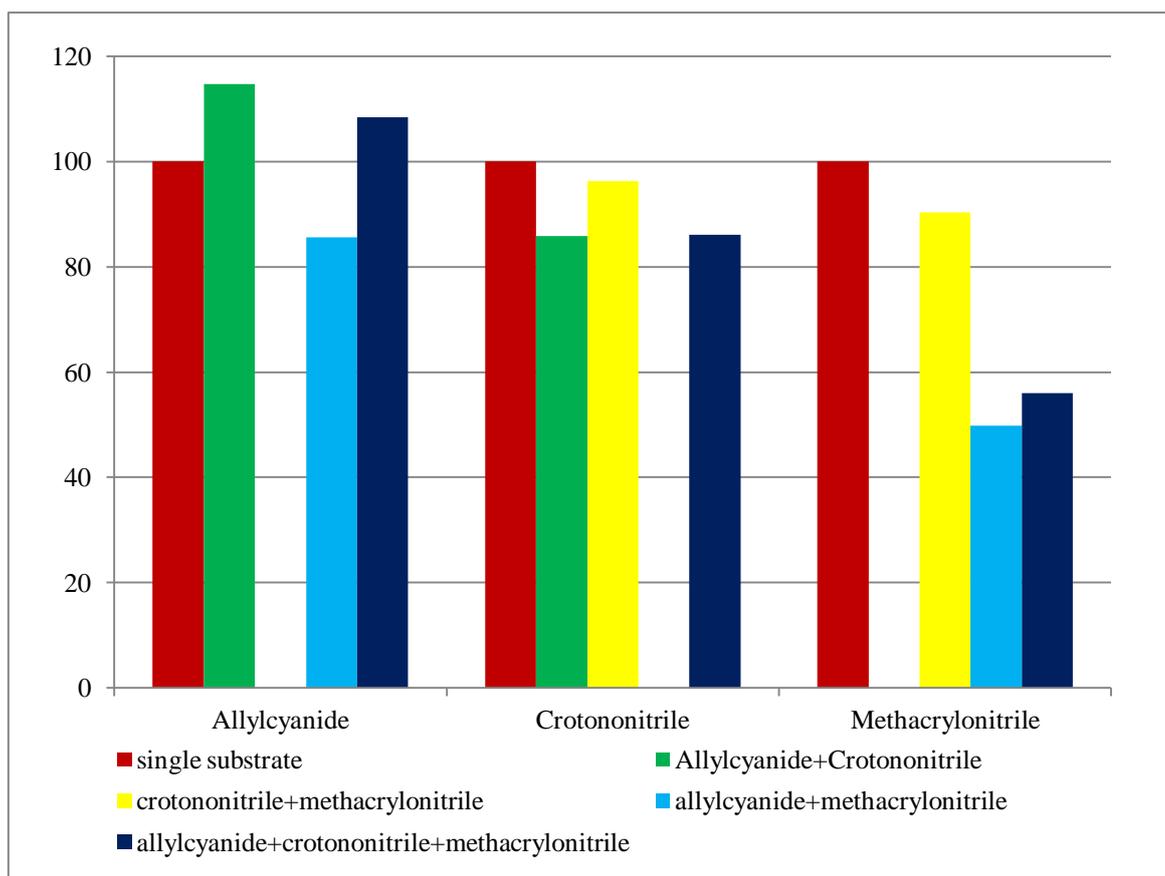


Figure 27- competitive hydrogenation for mixtures of reactants.

a- Allylcyanide + crotonitrile

In the presence of crotonitrile, the rate of allylcyanide hydrogenation was increased over that observed when allylcyanide reacted as a single substrate, whereas the rate of crotonitrile hydrogenation was reduced.

b- Methacrylonitrile + crotonitrile

When effect these two substrates were hydrogenated together their hydrogenation rates were reduced by a relatively small amount.

c- Allylcyanide + methacrylonitrile

When these two substrates were hydrogenated at the same time the conversion was significantly affected. In the presence of allylcyanide, methacrylonitrile conversion was decreased to almost half that observed for methacrylonitrile as a single substrate. The rate of hydrogenation of allylcyanide was also reduced but to a much lesser extent. The reaction profile is shown in figure 28.

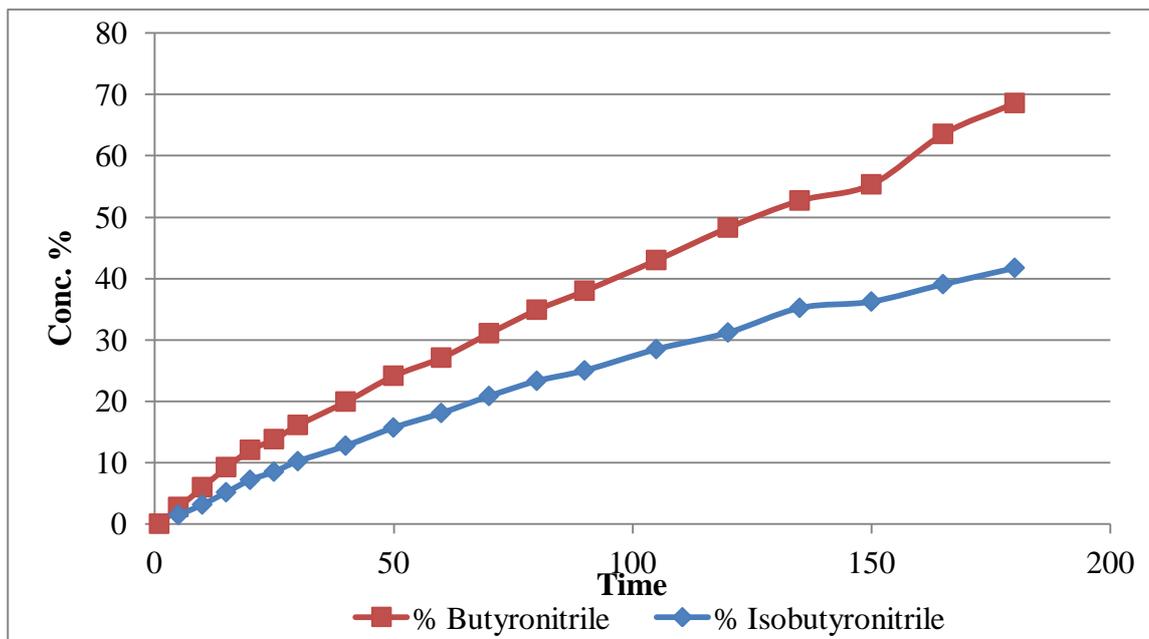


Figure 28- Product profile from allylcyanide + methacrylonitrile hydrogenation.

d- Allylcyanide + crotonitrile+ methacrylonitrile.

The conversion of allylcyanide was slightly enhanced by the presence of the other two substrates and was hydrogenated at a rate which was faster than the other two substrates. Crotonitrile reactivity was similar to that found when crotonitrile was reacted with allylcyanide in the absence of methacrylonitrile. Indeed the same behaviour was observed with methacrylonitrile which showed reactivity at the level found for the allylcyanide/methacrylonitrile reaction. The product profile is shown in figure 29.

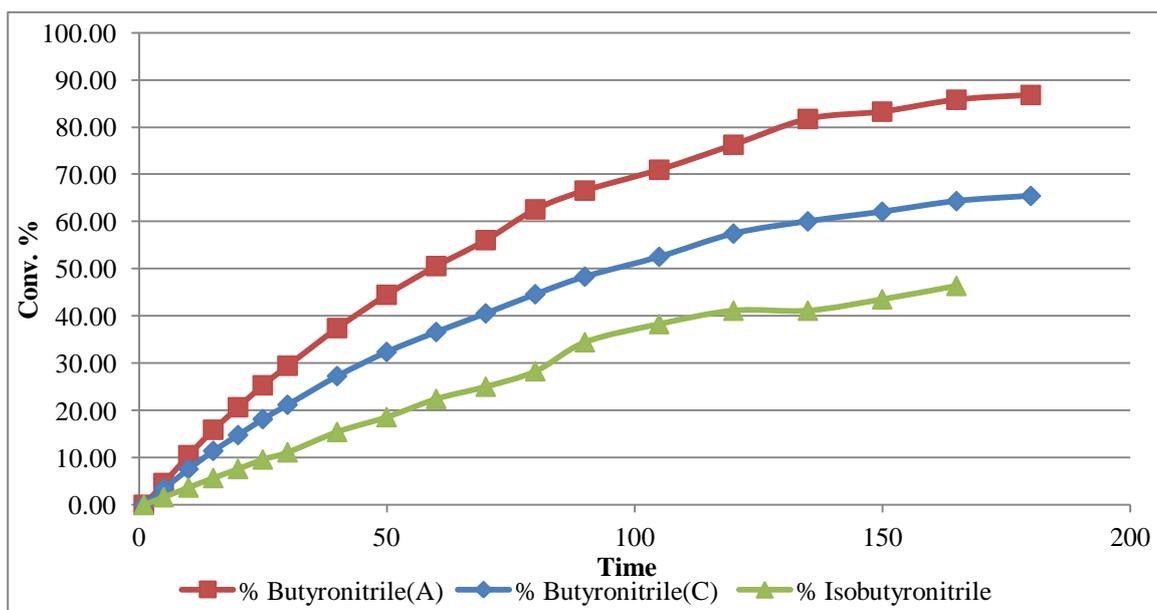


Figure 29- The three substrate mixture profile.

6. Discussion:

6.1 General introduction:

In this work four nitriles, namely, allylcyanide, cis- and trans-crotonitrile and methacrylonitrile, were hydrogenated over Pd/ θ -Al₂O₃. This group of reactants were chosen because they are all isomeric, unsaturated, C₄ nitriles that allow the investigation of electronic and steric factors in hydrogenation. All the reactions were carried out in a stirred tank reactor under a range of different reaction conditions (temperature, pressure, concentration and solvent) to allow as full an understanding as possible of the catalytic process. The only products detected were saturated nitriles, butyronitrile was obtained from allylcyanide and cis/trans-crotonitrile, while isobutyronitrile was obtained from methacrylonitrile. Results obtained from these tests were used to determine activation energies, reaction orders, rate constants and conversions. Competitive hydrogenation between the nitriles was also studied to give information on the relative strength of adsorption. These findings will be discussed in this section.

6.2 Kinetics:

The liquid phase hydrogenation of allylcyanide in IPA fitted a first order rate equation for temperatures of 30, 40 and 50°C. However as the temperature was raised the fit was less good and by 70°C, the reaction fitted a second order rate equation as shown in figures 18 and 19. The reason for this is likely to lie in a change of strength of adsorption with temperature. As the temperature is raised adsorption weakens, which can be reflected in a change in the kinetic order. For example in the hydrogenation of ethene over Cu/silica [71] the reaction order in ethene changed from -0.5 to 1 as the temperature was raised from 0°C to 200°C. Therefore as the temperature was increased to 60°C and 70°C and the adsorption of allylcyanide gets weaker the order moves from zero to first order allowing a fit to an overall second order reaction (approximately first order in both organic and hydrogen). Hence only the lower three temperatures (30, 40 and 50°C) were used for determining the activation energy. The activation energies calculated for the four nitriles are shown in table 21.

Table 21- Activation energies for the four nitriles.

Reactant	Allylcyanide	Methacrylonitrile	Crotonitrile	
			cis	trans
Activation Energy [kJ.mol ⁻¹]	20	50	46	40

Activation energy for allylcyanide was the lowest among the substrates. This result was expected as allylcyanide has a non-conjugated double bond (figure 30), which have been found to hydrogenate more easily than conjugated systems [31]. Nevertheless the value is lower than would be expected for an isolated C=C double bond (typically ~32 kJ.mol⁻¹).

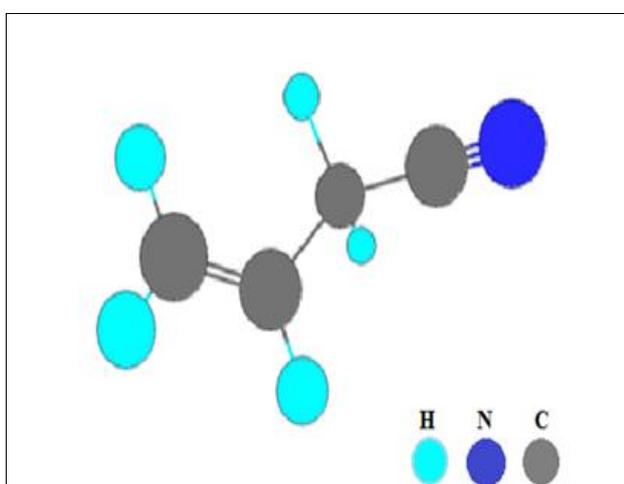


Figure 30- Allylcyanide structure.

The structure of cis-crotonitrile is shown in figure 31. Regarding the crotonitrile isomers, it was expected that trans-isomer might show higher stability as is the case for the 2-butenes (figure 32).

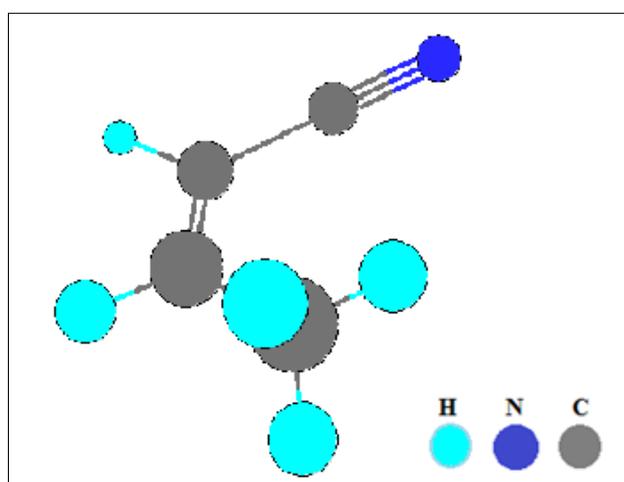


Figure 31- Cis-crotonitrile structure.

In our results the activation energy for the cis-isomer was slightly higher than trans-isomer which means that it needed higher energy to hydrogenate. This result is in agreement with the study by Lee and Zaera [62], who found that the isomerisation of trans-2-butene to cis-2-butene was easier on Pt(111) and related this increase of cis stability to the surface structure of the catalyst.

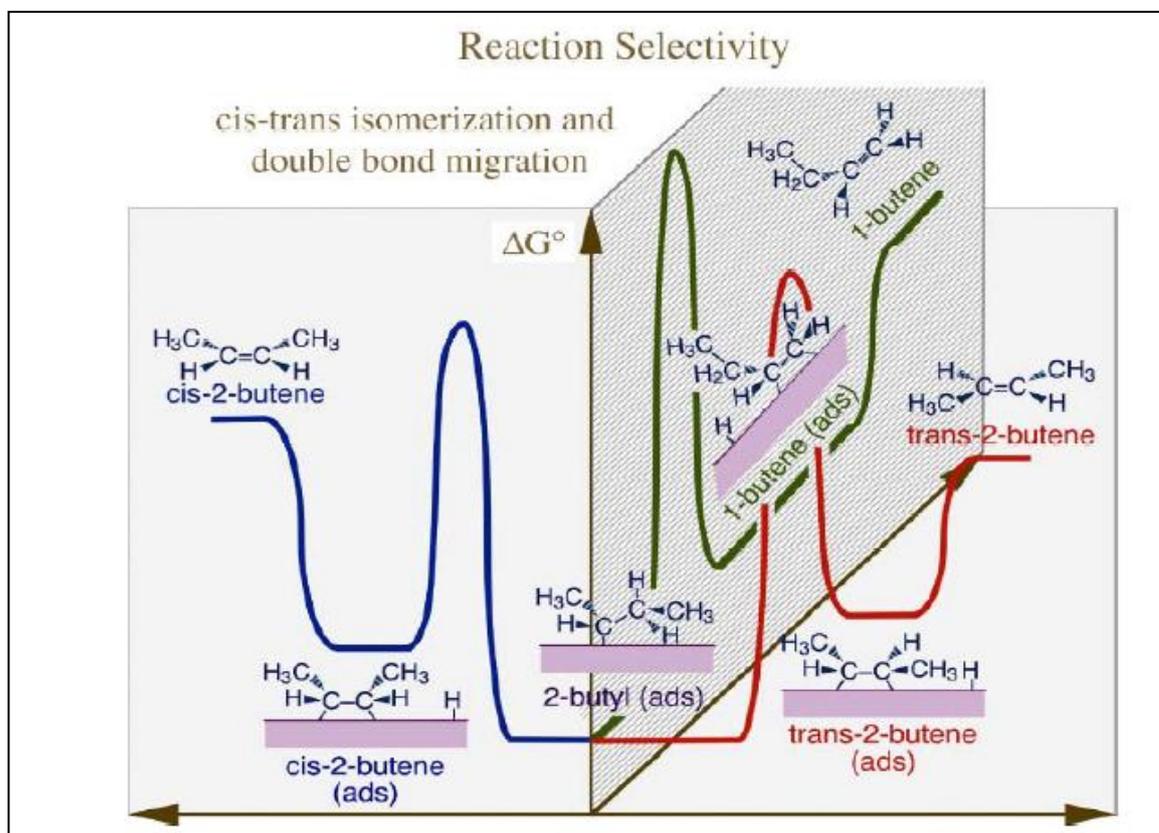


Figure 32- Energy diagram for the isomerisation of butenes on Pt [63].

As stated earlier the reaction order of double bond hydrogenation is temperature dependent and is often positive or first order in hydrogen and negative or zero order in substrate concentration at ambient temperatures. Cortright *et al.* [72] observed a variation of reaction order in the hydrogenation of ethylene over Pt that was dependent on temperature. The reaction orders varied between half and first order in hydrogen and between negative to zero order in ethylene. They found that as the temperature was increased to 100 °C the order in hydrogen increased from 0.5 order to 1. Furthermore, ethylene order changed from negative order to zero with increasing ethylene pressure. They suggested that at lower temperatures hydrogen and ethylene did not compete for the active sites: competitive adsorption was discovered at higher temperatures. In addition, the activation energy varied from 30 – 50 kJ mol⁻¹ [73]. Positive order in ethylene was also reported at higher ethylene pressure [39].

Our results showed that the orders in allylcyanide, *c/t*-crotonitrile and methacrylonitrile at 40°C were -1, 0.5 and 1 respectively. This indicates, as expected, that allylcyanide was strongly adsorbed while methacrylonitrile, the most sterically hindered reactant, was weakly adsorbed. These findings were in agreement with the findings of Béres *et al.* [74]. They investigated the interconversion of unsaturated C₄ nitriles (allylcyanide, crotonitrile and methacrylonitrile) over Na/NaY catalyst. They found that allylcyanide showed a higher reactivity where the lowest reactivity was shown in methacrylonitrile. These findings were attributed to the molecular structure of the unsaturated nitriles. In other words, crotonitrile and methacrylonitrile have a double bond conjugated with the nitrile group (figures 31 and 33) which makes them more stable and expected to show lower reactivity than allylcyanide which does not have a conjugation of the two unsaturated groups.

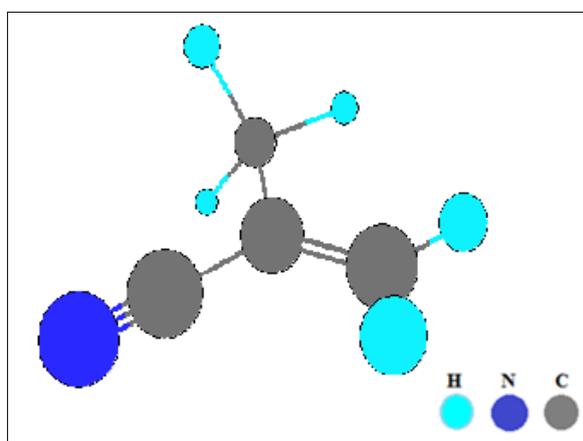


Figure 33- Methacrylonitrile structure.

The orders of reaction in hydrogen were 1, 0.5 and 1 for allylcyanide, crotonitrile and methacrylonitrile respectively. These values are typical for hydrogen orders where there is a strongly adsorbed reactant such as an alkene, alkyne or nitrile [73]. The variation of reaction order was explained by Rekoske *et al* [50]. They declared that the surface coverage is a key factor in altering reaction order. The reaction orders in hydrogen suggest that the surface coverage of hydrogen is low as is often found to be the case in alkene hydrogenation [73].

6.2.1 The effect of 1-propanol on reaction kinetics.

In order to find whether changing the solvent affected the kinetics of hydrogenation or not, the reaction order in the substrates was determined using IPA and 1-propanol as solvents. When IPA was used the orders in allylcyanide, crotonitrile and

methacrylonitrile were -1, 0.5 and 1 respectively. After using 1-propanol the order was 0.5 for allylcyanide and 1 for crotonitrile and methacrylonitrile indicating that changing the solvent did have an impact on reaction kinetics. Mukherjee and Vannice [19] studied the solvent effect on citral hydrogenation over Pt/SiO₂. They used eight solvents that were different in physical and electronic properties. The solvents were *n*-amyl acetate, ethyl acetate, *n*-hexane, cyclohexane, tetrahydrofuran, *p*-dioxane, ethanol and cyclohexanol. They found that the reaction order varied from 0.45 to 0.85 depending on the solvent used. Their finding did not follow the general thought that the order of a liquid phase hydrogenation for the substrate would be zero. They attributed the order variation to the amount of citral adsorbed on Pt surface. Our results would be in keeping with the concept that that 1-propanol adsorption competes with the adsorption of the reactants more effectively than IPA given that all of the nitriles have reaction orders that have moved to values that indicate a lower concentration on the surface.

6.3 Solvent effects.

In most of literature the solvent effect is attributed to the physical (hydrogen solubility) or the chemical nature of the solvent (e.g. acidity or polarity) [75]. After reviewing the values of dielectric constant for the solvents used in this work (table 22) it was clear that there was no direct effect of the solvent polarity on conversion. As shown on table 22 dodecane has the lowest dielectric constant value whereas 1-propanol has a significantly higher value yet both solvents show similar and low conversion patterns especially for allylcyanide.

Table 22- Dielectric constant and conversion.

Solvent	Conversion (%)			Dielectric Constant
	Allylcyanide	Methacrylonitrile	Crotonitrile	
IPA	80	83	76	17.9
1-Propanol	27	52	70	20.1
Acetone	82	86	78	20.7
Ethanol	65	90	82	24.5
Methanol	62	73	70	32.7
Dodecane	22	45	50	2

Allylcyanide was used as an example as shown on figure 34. Methanol has the highest value of dielectric constant but does not show a higher conversion compared to acetone or IPA. It is worth pointing out that the hydrogenation reaction did not continue for further hydrogenation with any solvent.

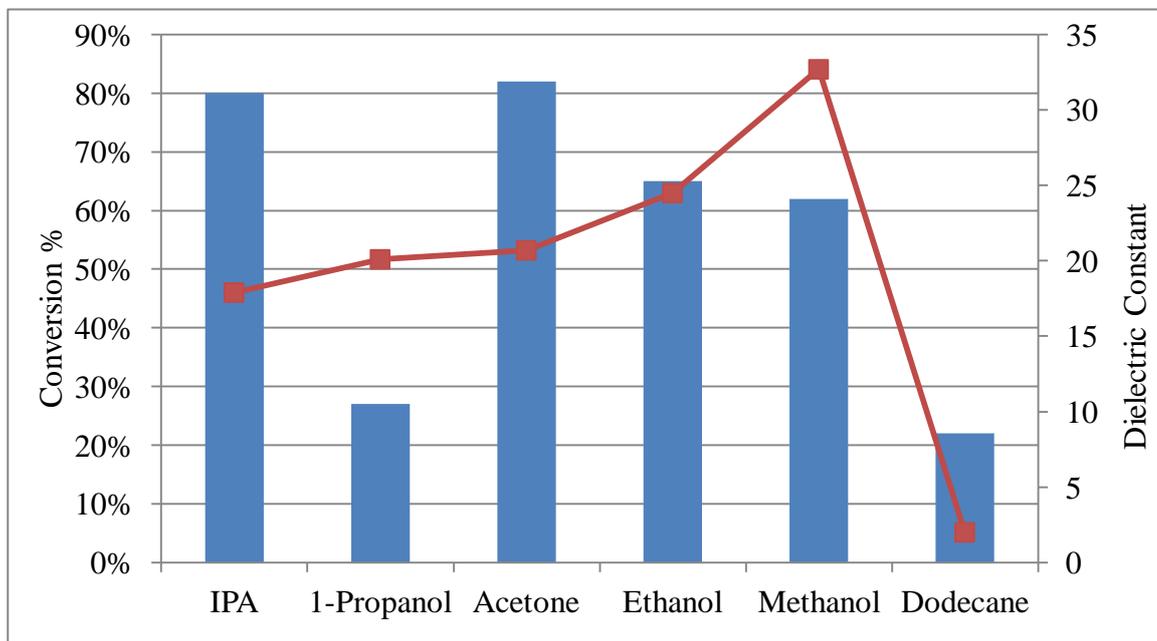


Figure 34- conversion of allylcyanide compared with dielectric constant for solvents used

In the literature most of the studies that discuss solvent effects do so by observing the behaviour on a single reactant. In these cases it is much easier to interpret the obtained results. The findings can more easily be attributed to physical or chemical properties such as hydrogen solubility and polarity of the solvent. It is more complicated to find a straightforward explanation for the solvent effect when considering various substrates. In this study three substrates were examined by using different solvents. Table 22 showed the conversion of allylcyanide, crotonitrile and methacrylonitrile by using different solvents namely isopropyl alcohol (IPA), 1-propanol, acetone, ethanol, methanol and dodecane. The results clearly showed an obvious fundamental difference not only when a different solvent is used, but also when using the same solvent for the three isomers. For example, by using 1-propanol only 27 % of allylcyanide was converted, while 70 % of crotonitrile was converted. When IPA and acetone were used as solvents there was a similarity in the conversion of the three isomers. This may be expected as the interconversion of IPA to acetone can be facile, hence any differences will be minimised. Another interesting point that worth mentioning is that for allylcyanide conversion when using 1-propanol and dodecane as solvents, both showed low conversion (27 % and 22 % respectively). When comparing dielectric constant values for the two solvents it was

found that 1-propanol dielectric constant (20) is much higher than the dielectric constant for dodecane (2). This alone conflicts with any idea of the effect of a solvent's dielectric constant influencing hydrogenation reactions. From the effect of 1-propanol on kinetics, it was suggested that 1-propanol was competing for sites with the substrates, which would explain the variation of the reaction order. On the other hand, dodecane which is a viscous liquid, should not compete for sites with the substrate but may have hydrogen solubility issues. Therefore the conversion similarity may be no more than a coincidence of two unrelated effects.

Similar comments could be made concerning a solubility effect. Conversions do not show an obvious pattern for the different substrates. It is suggested that the effect of solvent is attributed to the structure of substrate and the way that each substrate behaviour with solvents.

What has come out of our study on solvent effects is in good agreement with what has been stated recently by Bertero *et al* [76]. They said that, after analyzing a number of studies concerning the solvent effect, the general parameters that were used to explain the influence of solvent on hydrogenation was not complete and did not give a satisfactory interpretation. They suggested that it was important to give more attention to solvent interaction with the catalyst and also with the substrate hence giving more understanding of the nature of the solvent effect.

6.4 Isomerisation:

It is well documented that isomerisation is a possible side reaction when Pd is used as catalyst for olefins hydrogenation [60]. Boitiaux *et al.* [77] [78] [79] published a series of investigations on liquid phase hydrogenation of 1-butene, 1,3-butadiene and 1-butyne over Pd, Pt and Rh catalysts. In the case of 1-butyne they detected 2-butenes which were formed by isomerisation with different rates as shown on table 23 [78].

Table 23- 2-butenes/butane and trans/cis 2-butenes ratios [79]

Metal	2-butenes/butane	trans/cis 2-butenes
Pt	0.04	1.5
Pd	1.1	1.4
Rh	0.35	1.6

It is also documented that in the presence of another functional group such as in the case of diolefins isomerisation is strongly inhibited [80]. In the present work no isomerisation of any of the three substrates was detected. There are a number of possible reasons as to why this may occur. Firstly it may be due to the presence of two unsaturated groups, C=C and C≡N, with different types of proximity. Allylcyanoide has no conjugation between the two groups, crotonitrile has a conjugation system and methacrylonitrile has a conjugation system where the C=C bond is sterically hindered (figures 30, 31 and 33). Therefore allylcyanoide would isomerise to give a conjugated system (cis/trans-crotonitrile) while the reverse would be true for crotonitrile, although given the difference in stability it is unlikely that crotonitrile would isomerise to give allylcyanoide. This is in keeping with the study of the hydrogenation of 1,4-pentadiene and cis- and trans-1,3-pentadiene [81] where no isomerisation between isomers was observed. For methacrylonitrile to isomerise requires a breaking of a C-C bond as distinct from a C-H bond. Typically this type of isomerisation requires higher temperature and acid sites on the surface of the catalyst.

A further explanation for not observing any isomerisation behaviour for any of the substrates under study may be related to the presence of hydrogen in different locations of the metal crystallite. In recent publications [56] [57] [58] and [59], it was shown that the isomerisation reaction for alkenes is dependent on the way that hydrogen adsorbed on Pd surface. Subsurface hydrogen is responsible for hydrogenation whereas surface hydrogen leads to isomerisation. Figure 35 shows a scheme of the sites of surface and subsurface hydrogen on Pd [82]. Although various groups have concurred that the presence of subsurface hydrogen is required they have also noted that other aspects also effect the extent of this phenomenon. Doyle et al [56] compared the hydrogenation of ethylene and trans-pentene over Pd single crystal and Pd nanoparticles and they found that hydrogenation was only observed on Pd nanoparticles. They concluded that the presence of subsurface hydrogen was essential for hydrogenation to occur. The presence of subsurface hydrogen was attributed to the ability of nanoparticles to accommodate hydrogen easily because of the small size.

Wilde et al [83] came to the same conclusion that the presence of subsurface hydrogen is essential for the occurrence of hydrogenation. But, he attributed the hydrogen diffusion into Pd bulk to the carbonaceous deposits that were formed from the reactants on the surface of the catalyst. They suggested that these carbonaceous species were responsible for facilitating hydrogen diffusion.

Ludwig et al [61] also showed for the hydrogenation of cis 2-butene over Pd, that the presence of subsurface hydrogen is required to obtain the hydrogenation reaction. Otherwise, isomerisation is more likely to occur. They found that the catalyst surface containing low coordinated sites, corners or edges, is responsible for the diffusion of hydrogen to subsurface area of the metal, which enhance the hydrogenation reaction. Figure 36 shows a crystal surface indicating corner, edges and plane atoms. It was stated that terminal alkenes hydrogenation (or isomerisation) occurred on corner and edges of the catalyst. Whereas, the hydrogenation (or isomerisation) of internal alkenes occurred on the plane face of the catalyst [84]. In principle this may suggest that different sites are used by allylcyanide (and possibly methacrylonitrile) in comparison to crotonitrile. This will be discussed further in the competitive hydrogenation section. However for the position of hydrogen to explain the lack of isomerisation it would be necessary for most of the hydrogen present in the catalyst be subsurface. This seems unlikely as adsorption on the surface is required as a precursor to subsurface diffusion hence some surface hydrogen should be present and allow isomerisation.

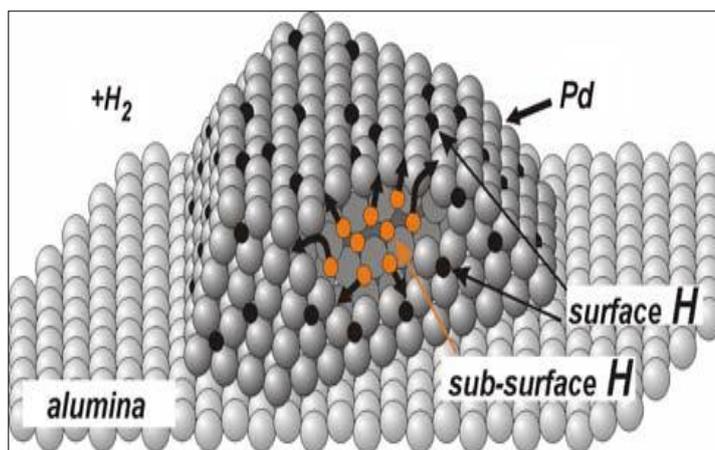


Figure 35- Scheme of surface and subsurface hydrogen on Pd.

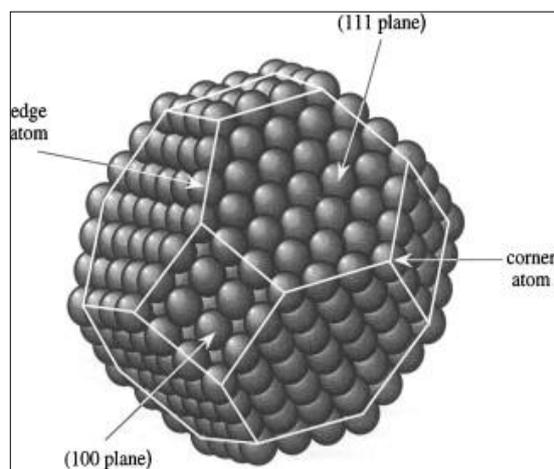


Figure 36- Corner, edge and plane atoms

An additional explanation which might clarify the absence of isomerisation reaction during the unsaturated nitriles reduction is the nature of the active site. Hu *et al.* [85] stated that adsorption and desorption mechanisms might be affected by the active sites acidity. Gluhoi *et al.* [86] investigated the support effect on the hydrogenation of acetonitrile over Ni and they found that condensation reactions were detected over the acid sites on the support. Furthermore, McGregor *et al.* [87] identified groups of active sites during the hydrogenation of pentenenitriles over Ni/Al₂O₃. One of these sites was identified as an acid site and it was shown to be responsible for pentenenitrile isomerisation. It is worth mentioning that the isomerisation reaction was not detected over Raney-Ni type catalysts, which suggest that this kind of reaction needs an acid or base site [36]. Indeed the isomerisation of C-4 nitriles has only been observed over strong base catalysts at high temperature. Beres *et al.* [74] found that using strong base catalysts such as Na/NaY at 623 K isomerisation was observed. Only such strong bases would catalyse methacrylonitrile isomerisation and even then no allylcyanide was formed, although the reverse isomerisation was detected. Weaker bases could catalyse allylcyanide/crotonitrile interconversion (double-bond migration) but not the formation of methacrylonitrile (C-C bond breaking).

6.5 Competitive hydrogenation:

In general, for the hydrogenation of alkenes over palladium catalysts the strength of adsorption of the alkene is much greater than hydrogen and hence the surface is normally considered to be completely covered by the substrate [73]. This is seen kinetically with a reaction order in the alkene of zero. In the case of competitive hydrogenation, where more than one substrate adsorb and react at the same time, the different molecules will

compete to occupy the catalyst surface. At the most basic level considering the Langmuir isotherm, the surface coverage of each reactant is influenced by the presence of any other reactant, e.g. $A + B \rightarrow C$ where C is non-adsorbing then we get $\theta_A = (bP)_A/[1+(bP)_A+(bP)_B]$ and a similar equation for θ_B revealing that the surface coverage of each substrate is dependent upon the pressure and adsorption coefficient of the other substrate. However even this does not reveal the full complexity as Langmuir assumes no interaction between adsorbed species. From the kinetic analysis a strength of adsorption order of allylcyanide > crotonitrile > methacrylonitrile can be proposed. Therefore we may expect this to influence the reaction chemistry. Previous studies [7] have shown that the position of C=C double bond is important to consider during the competitive hydrogenation. According to Molnar *et al.* [7] a terminal double bond is more reactive than other internal double bonds, a view also supported by Kačer and Červený [88].

Individually the reactivity of the isomers is very similar, however when added as pairs a definite trend is observed. In figure 27 and table 20 it was shown that the conversion of allylcyanide was only affected slightly by the other two substrates, whereas the reactivity of both crotonitrile and methacrylonitrile was considerably reduced when allylcyanide was present. These results would be in keeping with the suggestion that allylcyanide was more strongly adsorbed on the catalyst surface than the other isomers. In addition, methacrylonitrile, the most sterically hindered isomer, was affected considerably by the presence of the two other substrates. It was expected that allylcyanide would be the least affected by the presence of the other substrates. In a recent study Jackson *et al.* [89] showed for the competitive hydrogenation of 1-pentyne and 2-pentyne over Pd that the position of the triple bond had a significant effect over reactivity and selectivity. They concluded that terminal and internal alkynes were hydrogenated on different sites. Terminal alkynes were hydrogenated over corner and edges and internal ones were hydrogenated on plain face of the catalyst. The same was found to be true for alkenes. The isomerisation/hydrogenation of internal alkenes has been shown to occur on terrace and plane faces of Pd metal crystallites while isomerisation/hydrogenation of terminal alkenes has been shown to occur on edges and corners [89] [90] and [91]. Therefore allylcyanide may be hydrogenated on the edge/corner sites while crotonitrile and methacrylonitrile are hydrogenated on the plane faces. If this were to be the case then we would expect that allylcyanide hydrogenation would not be affected by the presence of the other isomers and that competitive hydrogenation between crotonitrile and

methacrylonitrile would result in a reduced activity for both systems. This is indeed what is observed. However this does not explain why the activity of both crotonitrile and methacrylonitrile is reduced when allylcyanoide is present.

It has been shown in various studies over palladium catalysts [57], [58] and [59] that sub-surface hydrogen is required to facilitate hydrogenation; surface hydrogen only facilitates isomerisation [56]. In a recent publication [61], Schauermaun and co-workers showed that for hydrogenation over palladium, fast diffusion of hydrogen into these sub-surface sites was required to sustain hydrogenation, however if this was inhibited, then isomerisation was observed but not hydrogenation. They also showed that rapid diffusion occurred via modified edge and corner sites. Therefore if the adsorbed terminal alkenyl nitrile inhibited the fast diffusion of hydrogen to the sub-surface by reacting with it, then we would expect the rate of hydrogenation of crotonitrile and methacrylonitrile to be reduced – as is observed.

Hence the alkenyl nitriles appear to behave in a manner inimical to alkenes in terms of hydrogenation of the C=C double bond, even though the presence of the nitrile function inhibits isomerisation.

7. Future work:

There are some aspects of this work that would benefit from further research. I have set out below some ideas for further research.

7.1 Catalyst and support:

It would be interesting to use other catalysts to compare between the activities of hydrogenation reactions over different metals, *e.g.* platinum or rhodium. In addition, as it has been suggested that the acidity/basicity of the support has an effect on controlling the reaction pathway (allowing isomerisation) testing catalysts with supports that vary in their acidity/basicity could also be investigated.

7.2 Solvent studies:

Since there was no obvious pattern to the solvent effect in this study, further studies on the effect of each solvent on kinetics and adsorption are required. Such as the kinetic studies that were made on IPA and the comparison between IPA and 1-propanol in this work.

7.3 Hydrogen presence:

There appears to be a relationship between the position where hydrogen is adsorbed (on the surface of the catalyst or into the subsurface) and this type of reaction behaviour. An investigation into the position of hydrogen on the catalyst to confirm these theories is also required.

7.4 Competitive hydrogenation:

It was suggested in this work that the structure of the substrate has a significant effect on the adsorption behaviour during the competitive hydrogenation. Therefore adsorption studies to confirm the difference the strength of adsorption and varying the ratios in the competitive hydrogenations would be revealing.

8. REFERENCES:

1. Berzelius JJ. Edinburgh new philosophical journal 1836;21:223.
2. Clark JH. Catalysis of organic reagents by supported inorganic reagents. New York: VCH; 1994.
3. Bowker M. The Basis and Applications of Heterogeneous Catalysis. Oxford: Oxford Science; 1998.
4. Navalikhina MD, Krylov OV. Heterogeneous hydrogenation catalysts. Russian Chemical Reviews 1998;67(7):587-616.
5. Wang Z. Sabatier-Senderens Reduction. Comprehensive Organic Name Reactions and Reagents: John Wiley & Sons, Inc.; 2010.
6. Zaera F. The surface chemistry of heterogeneous catalysis: Mechanisms, selectivity, and active sites. The Chemical Record 2005;5(3):133-44.
7. Molnar A, Sarkany A, Varga M. Hydrogenation of carbon-carbon multiple bonds: chemo-, regio- and stereo-selectivity. Journal of Molecular Catalysis A: Chemical 2001;173(1-2):185-221.
8. Satterfield CN. Heterogeneous catalysis in industrial practice. 2nd edition 1991.
9. Rylander PN. Hydrogenation Methods. UK, London: Academic Press; 1985.
10. Rylander PN. Catalytic hydrogenation in organic syntheses. New York: Academic Press.; 1979
11. Blaser H-U, Malan, C, Pugin, B, Spindler, F, Steiner, H, Studer, M. Selective Hydrogenation for Fine Chemicals: Recent Trends and New Developments. Advanced Synthesis & Catalysis 2003;345(1-2):103-51.
12. Augustine RL. Organic Functional Group Hydrogenation. Catalysis Reviews 1976 2012/01/10;13(1):285-316.
13. Gomez-Quero S, Cardenas-Lizana F, Keane MA. Effect of Metal Dispersion on the Liquid-Phase Hydrodechlorination of 2,4-Dichlorophenol over Pd/Al₂O₃. Industrial & Engineering Chemistry Research 2008 2012/01/11;47(18):6841-53.
14. Sautet P, Paul JF. Low temperature adsorption of ethylene and butadiene on platinum and palladium surfaces: A theoretical study of the di σ / π competition. Catalysis Letters 1991;9(3):245-60.
15. Albers P, Pietsch J, Parker SF. Poisoning and deactivation of palladium catalysts. Journal of Molecular Catalysis A: Chemical 2001;173(1-2):275-86.
16. Ertl G, Knözinger H, Weitkamp J. Handbook of heterogeneous catalysis. Weinheim: VCH; 1997.

17. Fajt V, Kurc L, Červený L. The effect of solvents on the rate of catalytic hydrogenation of 6-ethyl-1,2,3,4-tetrahydroanthracene-9,10-dione. *International Journal of Chemical Kinetics*2008;40(5):240-52.
18. Cerveny L, Ruzicka V. Competitive Catalytic Hydrogenation in the Liquid Phase on Solid Catalysts. *Catalysis Reviews*1982 2012/01/08;24(4):503-66.
19. Mukherjee S, Vannice MA. Solvent effects in liquid-phase reactions: I. Activity and selectivity during citral hydrogenation on Pt/SiO₂ and evaluation of mass transfer effects. *Journal of Catalysis*2006;243(1):108-30.
20. Rajadhyaksha RA, Karwa SL. Solvent effects in catalytic hydrogenation. *Chemical Engineering Science*1986;41(7):1765-70.
21. Kishida S, Teranishi S. Kinetics of liquid-phase hydrogenation of acetone over Raney nickel catalyst. *Journal of Catalysis*1968;12(1):90-6.
22. Gamez A, Kohler J, Bradley J. Solvent effects in the kinetics of the enantioselective hydrogenation of ethyl pyruvate. *Catalysis Letters*1998;55(2):73-7.
23. Augustine RL, Techasauvapak P. Heterogeneous catalysis in organic synthesis. Part 9. Specific site solvent effects in catalytic hydrogenations. *Journal of Molecular Catalysis*1994;87(1):95-105.
24. Hajek J, Kumar, N, Maki-Arvela, P, Salmi, T, and Murzin, DY. Selective hydrogenation of cinnamaldehyde over Ru/Y zeolite. *Journal of Molecular Catalysis A: Chemical*2004;217(1-2):145-54.
25. Augustine RL, Warner RW, Melnick MJ. Heterogeneous catalysis in organic chemistry. 3. Competitive adsorption of solvents during alkene hydrogenations. *The Journal of Organic Chemistry*1984 2011/12/23;49(25):4853-6.
26. Toukoniitty EM-A, P. Kuusisto, J. Nieminen, V. Paivarinta, J. Hotokka, M. Salmi, T. Murzin, DY. Solvent effects in enantioselective hydrogenation of 1-phenyl-1,2-propanedione. *Journal of Molecular Catalysis A: Chemical*2003;192:135-51.
27. Panpranot JP, Kunnika. P, Piyasan. H, Masashi. F, Shin-ichiro. Arai, M. A comparative study of liquid-phase hydrogenation on Pd/SiO₂ in organic solvents and under pressurized carbon dioxide: Activity change and metal leaching/sintering. *Journal of Molecular Catalysis A: Chemical*2006;253:20-4.
28. Adkins H. Hydrogenation Role Of The Catalyst. *Industrial & Engineering Chemistry*1940 2012/02/21;32(9):1189-92.
29. Nishimura S. *Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis*. John Wiley & Sons; 2001. p. 773.
30. Mathison IW, Fowler WL. Hydrogenation of substituted isoquinolines over nickel catalyst I: The effects of pressure and temperature on the hydrogenation of 5-nitro-2-alkylisoquinolinium salts. *Journal of Pharmaceutical Sciences*1969;58(10):1238-41.

31. Singh UK, Vannice MA. Kinetics of liquid-phase hydrogenation reactions over supported metal catalysts - a review. *Applied Catalysis A: General*2001;213(1):1-24.
32. Kalantri PB, Chandalia SB. Kinetics of liquid-phase reduction of o-nitroaniline to o-phenylenediamine by hydrogen in methanol using palladium/carbon as catalyst. *Industrial & Engineering Chemistry Process Design and Development*1982 2012/01/30;21(1):186-8.
33. Guo XC, Madix RJ. Selective Hydrogenation and H-D Exchange of Unsaturated Hydrocarbons on Pd(100)-P(1 $\bar{1}$ —1)-H(D). *Journal of Catalysis*1995;155(2):336-44.
34. Ouchaib T, Massardier J, Renouprez A. Competitive hydrogenation of butadiene and butene on palladium and platinum catalysts. *Journal of Catalysis*1989;119(2):517-20.
35. Kukula P, Studer M, Blaser H-U. Chemoselective Hydrogenation of α,β -Unsaturated Nitriles. *Advanced Synthesis & Catalysis*2004;346(12):1487-93.
36. Kukula P, Koprivova K. Structure-selectivity relationship in the chemoselective hydrogenation of unsaturated nitriles. *Journal of Catalysis*2005;234(1):161-71.
37. Schäringer P, Müller TE, Lercher JA. Investigations into the mechanism of the liquid-phase hydrogenation of nitriles over Raney-Co catalysts. *Journal of Catalysis*2008;253(1):167-79.
38. Neurock M, van Santen RA. A First Principles Analysis of C-H Bond Formation in Ethylene Hydrogenation. *The Journal of Physical Chemistry B*2000 2012/04/23;104(47):11127-45.
39. Hansen EW, Neurock M. First-Principles-Based Monte Carlo Simulation of Ethylene Hydrogenation Kinetics on Pd. *Journal of Catalysis*2000;196(2):241-52.
40. Horiuti I, Polanyi M. Exchange reactions of hydrogen on metallic catalysts. *Transactions of the Faraday Society*1934;30.
41. Mohsin SB, Trenary M, Robota HJ. Infrared identification of the low-temperature forms of ethylene adsorbed on platinum/alumina. *The Journal of Physical Chemistry*1988 2012/04/22;92(18):5229-33.
42. Cremer PS, Su, X, Shen, YR, Somorjai, GA. Ethylene Hydrogenation on Pt(111) Monitored in Situ at High Pressures Using Sum Frequency Generation. *Journal of the American Chemical Society*1996 2012/04/04;118(12):2942-9.
43. Lee TR, Whitesides GM. Heterogeneous, platinum-catalyzed hydrogenations of (diolefin)dialkylplatinum(II) complexes. *Accounts of Chemical Research*1992 2012/02/29;25(6):266-72.
44. Stacchiola D, Tysoe WT. The Kinetics of Ethylidyne Formation from Ethylene on Pd(111). *The Journal of Physical Chemistry C*2009 2012/04/19;113(19):8000-1.

45. Santen RA, Neurock M. *Molecular Heterogeneous Catalysis: A Conceptual and Computational Approach*: Wiley-VCH; 2006.
46. Fahmi A, van Santen RA. Density Functional Study of Ethylene Adsorption on Palladium Clusters. *The Journal of Physical Chemistry* 1996 2012/04/19;100(14):5676-80.
47. Shaikhutdinov SK, Heemeier, M, Baumer, M, Lear, T, Lennon, D, Oldman, RJ, Jackson, SD, Freund, H. J. Structure-Reactivity Relationships on Supported Metal Model Catalysts: Adsorption and Reaction of Ethene and Hydrogen on Pd/Al₂O₃/NiAl(110). *Journal of Catalysis* 2001;200(2):330-9.
48. Beebe TP, Yates JT. An in situ infrared spectroscopic investigation of the role of ethylidyne in the ethylene hydrogenation reaction on palladium/alumina. *Journal of the American Chemical Society* 1986 2012/04/17;108(4):663-71.
49. Davis SM, Zaera F, Gordon BE, Somorjai GA. Radiotracer and thermal desorption studies of dehydrogenation and atmospheric hydrogenation of organic fragments obtained from [14C]ethylene chemisorbed over Pt(111) surfaces. *Journal of Catalysis* 1985;92(2):240-6.
50. Rekoske JE, Cortright, RD., Goddard, SA., Sharma, SB. and Dumesic, JA. Microkinetic analysis of diverse experimental data for ethylene hydrogenation on platinum. *The Journal of Physical Chemistry* 1992 2012/04/22;96(4):1880-8.
51. Vladimir P, Geoffrey CB. Chapter 11 Catalytic hydrogenation and dehydrogenation. *Studies in Surface Science and Catalysis*: Elsevier; 1995. p. 477-539.
52. Smith GV, Notheisz F. Chapter 2 - Hydrogenations. *Heterogeneous Catalysis in Organic Chemistry*. San Diego: Academic Press; 1999. p. 29-96.
53. Oro LA, Carmona D, Fraile JM. Chapter 3 Hydrogenation Reactions. *Metal-Catalysis in Industrial Organic Processes*: The Royal Society of Chemistry; 2006. p. 79-113.
54. Musolino MG, Caia, CV., Mauriello, F, Pietropaolo, R. Hydrogenation versus isomerization in the reaction of cis-2-butene-1,4-diol over supported catalysts: The role of Group VIII transition metals in driving the products selectivity. *Applied Catalysis A: General* 2010;390(1-2):141-7.
55. Hub S, Hilaire L, Touroude R. Hydrogenation of But-1-yne and But-1-ene on Palladium Catalysts: Particle Size Effect. *Applied Catalysis* 1988;36(0):307-22.
56. Doyle AM, Shaikhutdinov, SK., Jackson, SD, Freund, H-J. Hydrogenation on Metal Surfaces: Why are Nanoparticles More Active than Single Crystals? *Angewandte Chemie International Edition* 2003;42(42):5240-3.
57. Brandt B, Fischer, J-H, Ludwig, W, Libuda, J, Zaera, F, Schauermaun, S, Freund, H-J. Isomerization and Hydrogenation of cis-2-Butene on Pd Model Catalyst. *The Journal of Physical Chemistry C* 2008 2012/05/19;112(30):11408-20.

58. Doyle AM, Shaikhutdinov SK, Freund H-J. Alkene chemistry on the palladium surface: nanoparticles vs single crystals. *Journal of Catalysis*2004;223(2):444-53.
59. Wood J, Bodenes, L, Bennett, J, Deplanche, K, Macaskie, LE. Hydrogenation of 2-Butyne-1,4-diol Using Novel Bio-Palladium Catalysts. *Industrial & Engineering Chemistry Research*2009 2012/05/17;49(3):980-8.
60. Augustine RL, Yaghmaie F, Van Peppen JF. Heterogeneous catalysis in organic chemistry. 2. A mechanistic comparison of noble-metal catalysts in olefin hydrogenation. *The Journal of Organic Chemistry*1984 2011/12/24;49(11):1865-70.
61. Ludwig W, Savara, A, Dostert, K-H, Schauermaun, S. Olefin hydrogenation on Pd model supported catalysts: New mechanistic insights. *Journal of Catalysis*2011;284(2):148-56.
62. Lee I, Zaera F. Selectivity in Platinum-Catalyzed cis-trans Carbon-Carbon Double-Bond Isomerization. *Journal of the American Chemical Society*2005 2012/06/03;127(35):12174-5.
63. Ma Z, Zaera F. Organic chemistry on solid surfaces. *Surface Science Reports*2006;61(5):229-81.
64. Sivasankar N, Prins R. Reactions of mixed dialkyl- and trialkylamines over Pd/Al₂O₃. *Journal of Catalysis*2006;241(2):342-55.
65. Barrault J, Pouilloux Y. Synthesis of fatty amines. Selectivity control in presence of multifunctional catalysts. *Catalysis Today*1997;37(2):137-53.
66. Kukula P, Gabova, V, Koprivova, K, Trtik, P. Selective hydrogenation of unsaturated nitriles to unsaturated amines over amorphous CoB and NiB alloys doped with chromium. *Catalysis Today*2007;121(1-2):27-38.
67. Chorkendorff I, Niemantsverdriet JW. Concepts of modern catalysis and kinetics: Wiley-VCH; 2003.
68. Kenneth S. The use of nitrogen adsorption for the characterisation of porous materials. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*2001;187-188(0):3-9.
69. Stevens B. Chemical kinetics for general students of chemistry. London: Chapman and Hall; 1970.
70. Atkins PW. The elements of physical chemistry. 3 ed: Oxford University Press; 2001.
71. Jackson SD, Robertson FJ, Willis J. A study of copper/silica catalysts: reduction, adsorption and reaction. *Journal of Molecular Catalysis*1990;63(2):255-68.
72. Cortright RDG, Scott A. Rekoske, JE. and Dumesic, JA. Kinetic study of ethylene hydrogenation. *Journal of Catalysis*1991;127(1):342-53.

73. Bond GC. Metal-catalysed reactions of hydrocarbons: Springer Science; 2005.
74. Attila Béres ZK, Hannus, I, Molnár, A, and Kricsi, I. Interconversion of unsaturated C4 nitriles under basic conditions II. Catalytic and FTIR study over basic zeolites. *Applied Catalysis A: General*1996;146(2):331-8.
75. de Bellefon C, Fouilloux P. Homogeneous and Heterogeneous Hydrogenation of Nitriles in a Liquid Phase: Chemical, Mechanistic, and Catalytic Aspects. *Catalysis Reviews*1994 2012/01/12;36(3):459-506.
76. Bertero NM, Trasarti, AF, Apesteguía, CR. and Marchi, AJ. Solvent effect in the liquid-phase hydrogenation of acetophenone over Ni/SiO₂: A comprehensive study of the phenomenon. *Applied Catalysis A: General*2011;394(1-2):228-38.
77. Boitiaux JP, Cosyns J, Robert E. Liquid phase hydrogenation of unsaturated hydrocarbons on palladium, platinum and rhodium catalysts. Part I: kinetic study of 1-butene, 1,3-butadiene and 1-butyne hydrogenation on platinum. *Applied Catalysis*1987;32(0):145-68.
78. Boitiaux JP, Cosyns J, Robert E. Liquid phase hydrogenation of unsaturated hydrocarbons on palladium, platinum and rhodium catalysts. Part II: kinetic study of 1-butene, 1,3-butadiene and 1-butyne hydrogenation on rhodium; comparison with platinum and palladium. *Applied Catalysis*1987;32(0):169-83.
79. Boitiaux JP, Cosyns J, Robert E. Hydrogenation of unsaturated hydrocarbons in liquid phase on palladium, platinum and rhodium catalysts: III. Quantitative Selectivity Ranking of Platinum, Palladium and Rhodium in the Hydrogenation of 1-Butene, 1,3-Butadiene and 1-Butyne Using a Single Reaction Scheme. *Applied Catalysis*1987;35(2):193-209.
80. Boitiaux JP, Cosyns J, Vasudevan S. Hydrogenation of highly unsaturated hydrocarbons over highly dispersed palladium catalyst: Part I: behaviour of small metal particles. *Applied Catalysis*1983;6(1):41-51.
81. Jackson SD, Monaghan A. Hydrogenation of unsaturated hydrocarbons-40 years on: Hydrogenation of 1,3-pentadiene over Pd/alumina. *Catalysis Today*2007;128(1-2):47-51.
82. Freund H-J. Model Systems in Heterogeneous Catalysis: Selectivity Studies at the Atomic Level. *Topics in Catalysis*2008;48(1):137-44.
83. Wilde M, Fukutani, K, Ludwig, W, Brandt, B, Fischer, J-H, Schauer mann, S, and Freund, H-J. Influence of Carbon Deposition on the Hydrogen Distribution in Pd Nanoparticles and Their Reactivity in Olefin Hydrogenation. *Angewandte Chemie International Edition*2008;47(48):9289-93.
84. Begley LC, Kakanskas, KJ., Monaghan, A, Jackson, SD. Effect of molecular structure on the hydrogenation and isomerisation of propenylbenzene isomers. *Catalysis Science & Technology*2012;2(6):1287-91.

85. Hu S, Xue, M, Chen, H, and Shen, J. The effect of surface acidic and basic properties on the hydrogenation of aromatic rings over the supported nickel catalysts. *Chemical Engineering Journal*2010;162(1):371-9.
86. Gluhoi AC, Mărginean P, Stănescu U. Effect of supports on the activity of nickel catalysts in acetonitrile hydrogenation. *Applied Catalysis A: General*2005;294(2):208-14.
87. McGregor J, Canning, AS., Mitchell, S, Jackson, SD and Gladden, LF. The influence of carbon laydown on selectivity in the hydrogenation of pentenenitriles over supported-nickel catalysts. *Applied Catalysis A: General*2010;384(1-2):192-200.
88. Kačer P, Červený L. Structure effects in hydrogenation reactions on noble metal catalysts. *Applied Catalysis A: General*2002;229(1-2):193-216.
89. Jackson SD, Garcia, PE., Lynch, AS. and Monaghan, A. Using modifiers to specify stereochemistry and enhance selectivity and activity in palladium-catalysed, liquid phase hydrogenation of alkynes. *Catalysis Today*2011;164(1):548-51.
90. Doyle AM, Shaikhutdinov SK, Freund H-J. Surface-Bonded Precursor Determines Particle Size Effects for Alkene Hydrogenation on Palladium. *Angewandte Chemie International Edition*2005;44(4):629-31.
91. Anderson JA, Mellor J, Wells RPK. Pd catalysed hexyne hydrogenation modified by Bi and by Pb. *Journal of Catalysis*2009;261(2):208-16.

9. Appendix:

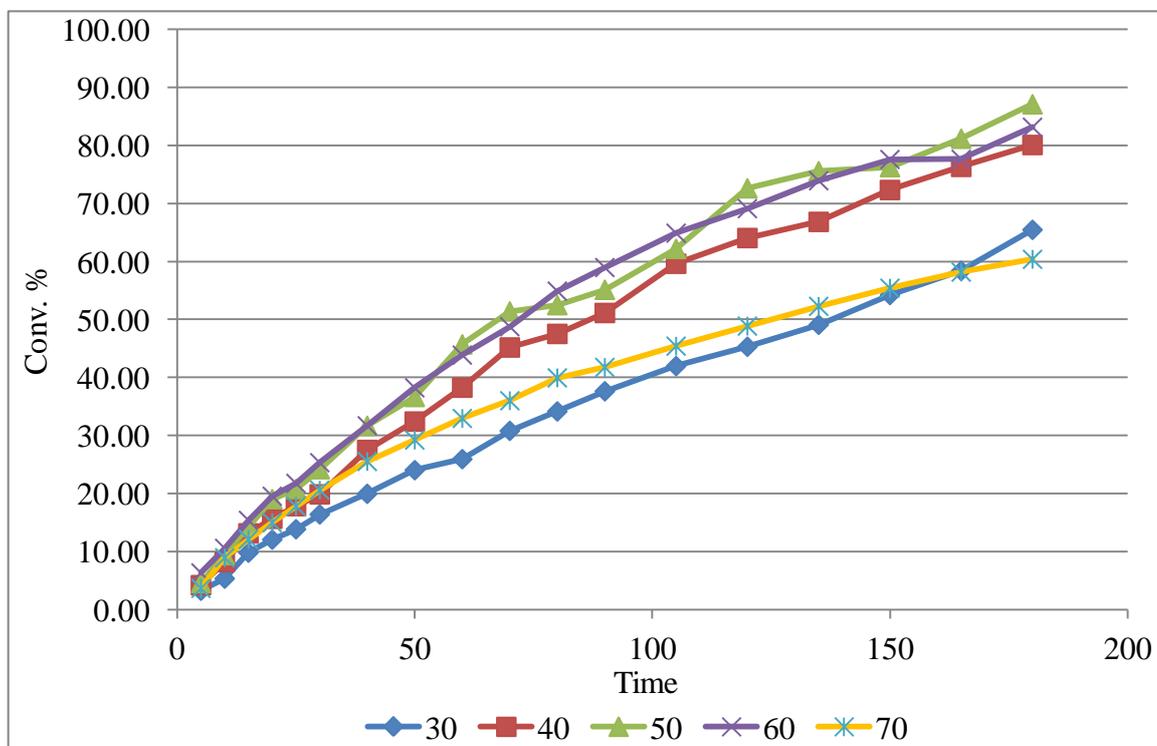
In order to determine activation energies and order of reactions depending on hydrogen pressure and substrate concentration, a series of reaction were performed with different reaction parameters (temperature, pressure and reactant volume). This appendix contains the basic data for conversion for all the reactions undertaken to generate the kinetic parameters.

All these reaction were carried out using IPA as a solvent.

ALLYLCYANIDE:

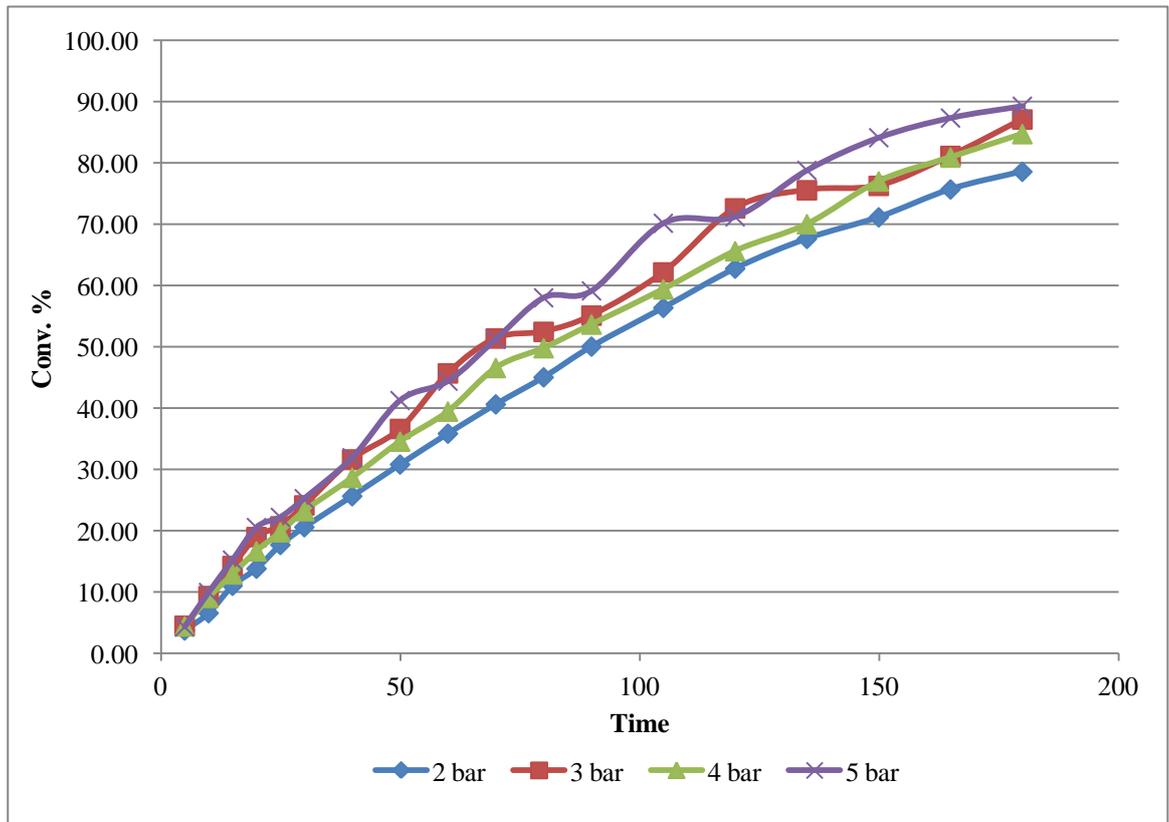
Temperature effect:

Time \ temp.	30 °C	40 °C	50 °C	60 °C	70 °C
% Butyronitrile					
5	3	4	4	6	3
10	5	8	9	10	8
15	9	13	14	15	12
20	12	15	19	19	14
25	13	17	20	21	17
30	16	19	24	25	20
40	19	27	31	31	25
50	24	32	36	38	29
60	25	38	45	43	32
70	30	45	51	48	36
80	34	47	52	54	39
90	37	51	55	58	41
105	41	59	62	64	45
120	45	64	72	69	48
135	49	66	75	73	52
150	54	72	76	77	55
165	58	76	81	77	58
180	65	80	87	83	60



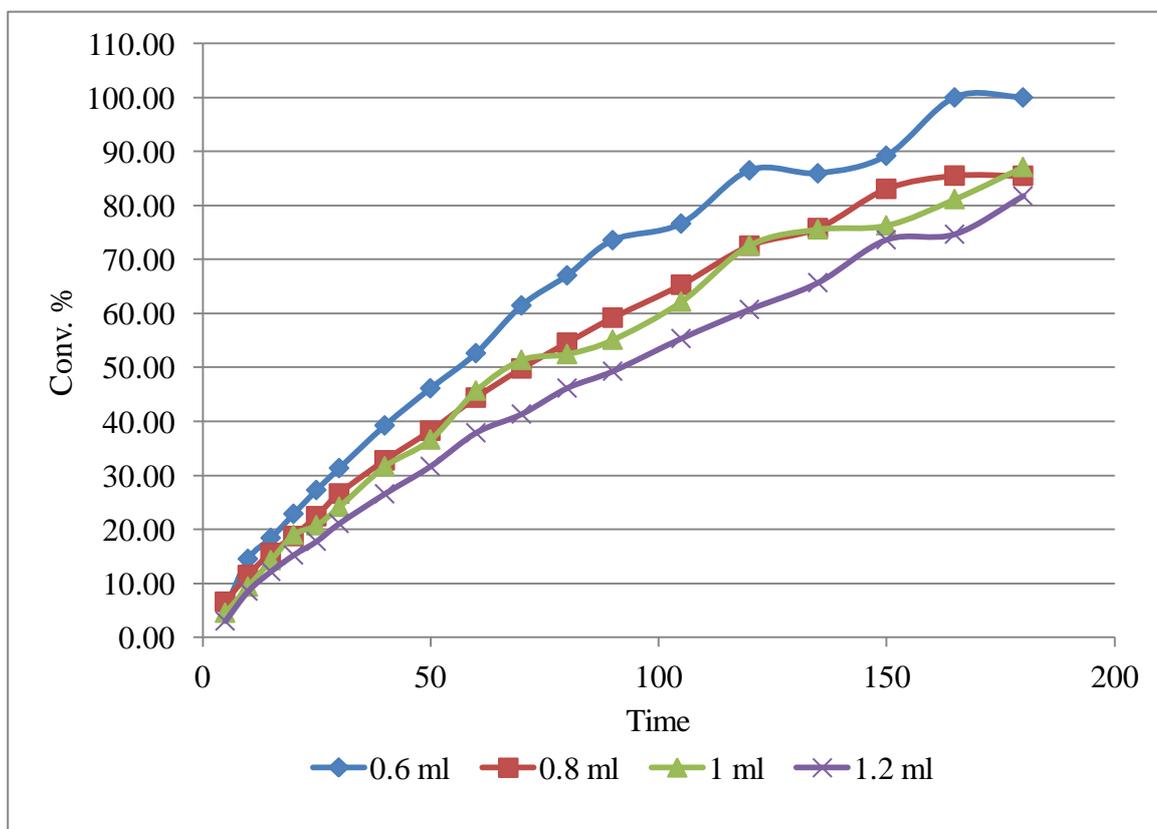
Pressure effect:

Time \ pressure	2 bar	3 bar	4 bar	5 bar
5	3	4	4	4
10	6	9	9	10
15	11	14	12	15
20	13	19	16	20
25	17	20	19	22
30	20	24	23	25
40	25	31	28	31
50	30	36	34	41
60	35	45	39	44
70	40	51	46	51
80	45	52	49	58
90	50	55	53	59
105	56	62	59	70
120	62	72	65	71
135	67	75	70	78
150	71	76	77	84
165	75	81	80	87
180	78	87	84	89



Concentration effect:

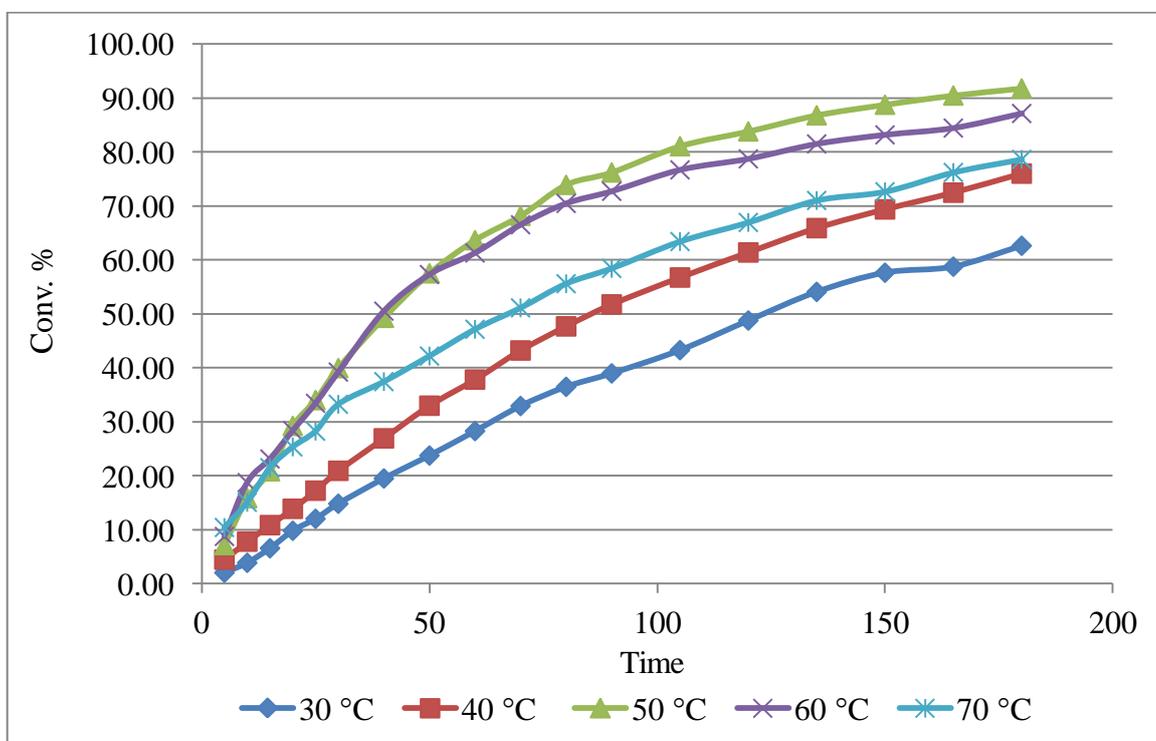
Time \ Conc.	0.6 ml	0.8 ml	1 ml	1.2 ml
5	5	6	4	3.03
10	14	11	9	8
15	18	15	14	12
20	22	18	19	15
25	27	22	20	17
30	31	26	24	21
40	39	32	31	26
50	46	38	36	31
60	52	44	45	37
70	61	49	51	41
80	67	54	52	46
90	73	59	55	49
105	76	65	62	55
120	86	72	72	60
135	85	75	75	65
150	89	83	76	73
165	100	85	81	74
180	100	85	87	81



CROTONITRILE:

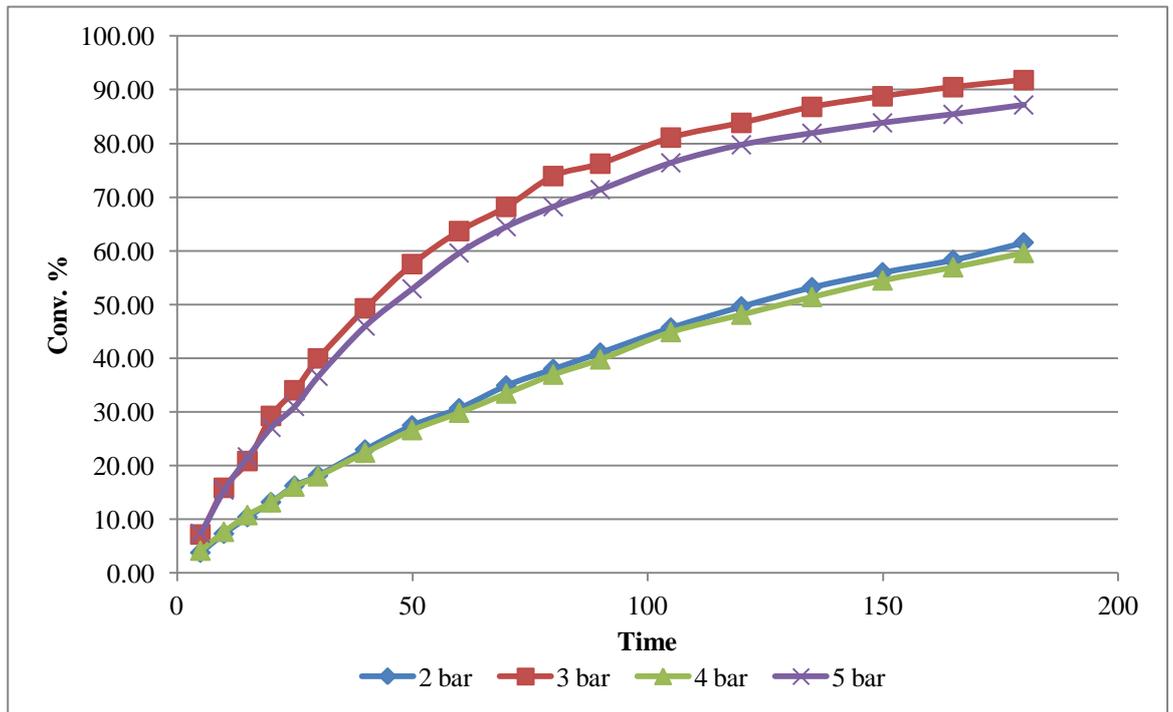
Temperature effect:

temp. Time	30 °C	40 °C	50 °C	60 °C	70 °C
5	2	4	7	8	10
10	3	7	15	18	15
15	6	10	20	23	21
20	9	13	29	28	25
25	12	17	34	33	28
30	14	20	39	39	33
40	19	26	49	50	37
50	23	33	57	57	42
60	28	37	63	61	47
70	32	43	68	66	51
80	36	47	73	70	55
90	38	51	76	72	58
105	43	56	81	76	63
120	48	61	83	78	66
135	54	65	86	81	71
150	57	69	88	83	72
165	58	72	90	84	76
180	62	76	91	87	78



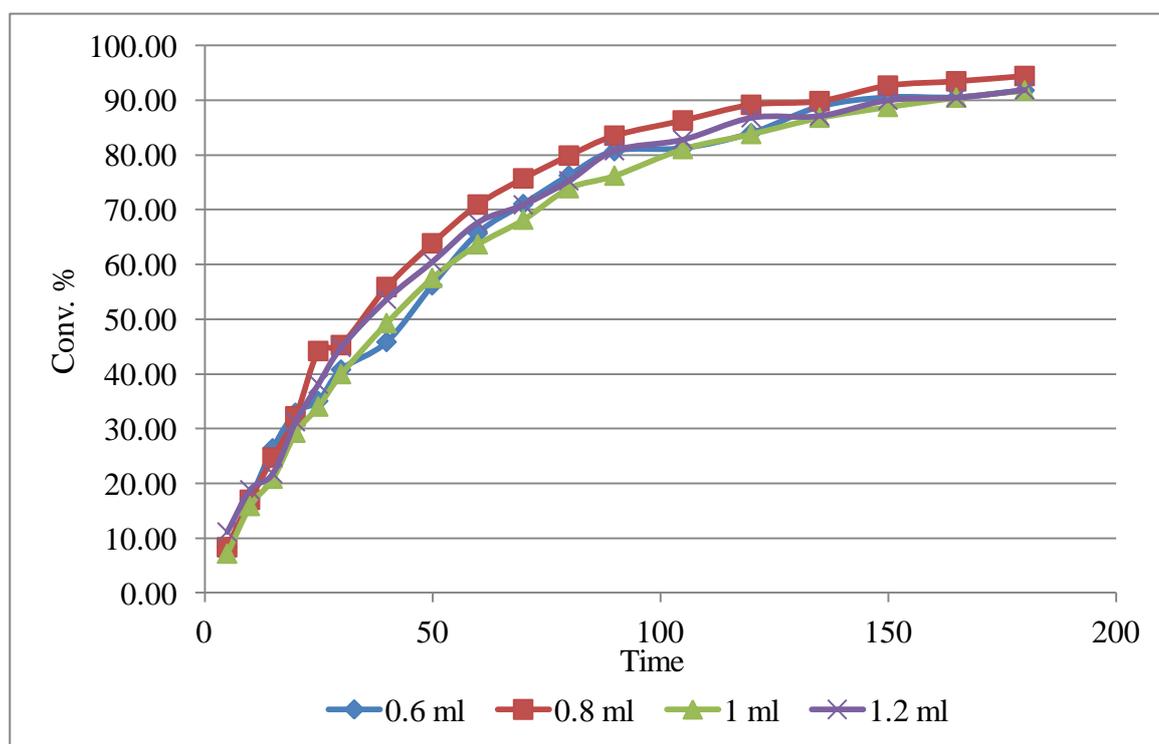
Pressure effect:

Time \ pressure	2 bar	3 bar	4 bar	5 bar
5	3	7	4	7
10	7	15	7	15
15	10	20	10	21
20	13	29	13	27
25	16	34	16	31
30	18	39	18	36
40	23	49	22	45
50	27	57	26	52
60	30	63	29	59
70	34	68	33	64
80	38	73	36	68
90	41	76	39	71
105	45	81	44	76
120	49	83	48	79
135	53	86	51	81
150	56	88	54	83
165	58	90	56	85
180	61	91	59	87



Concentration effect:

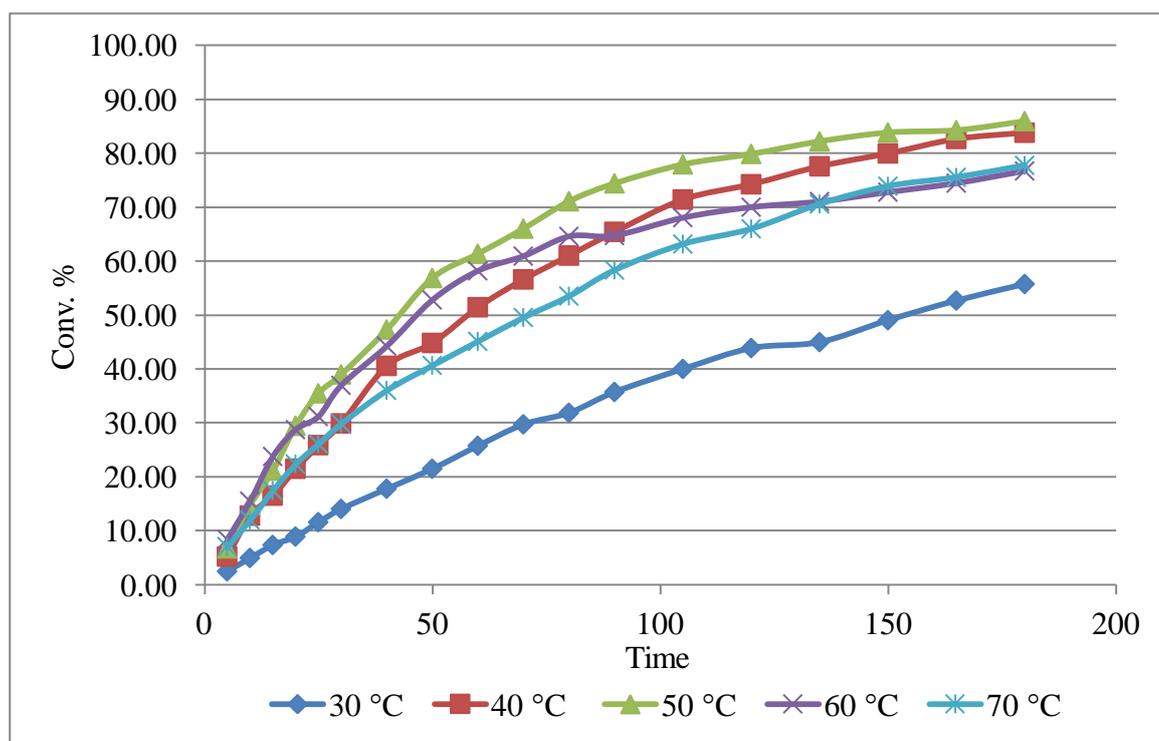
Time \ Conc.	0.6 ml	0.8 ml	1 ml	1.2 ml
5	8	8	7	11
10	17	17	15	18
15	26	24	20	21
20	32	32	29	31
25	35	44	34	38
30	40	45	39	44
40	45	55	49	53
50	56	63	57	60
60	65	70	63	67
70	71	75	68	70
80	76	79	73	75
90	80	83	76	80
105	81	86	81	82
120	83	89	83	86
135	88	89	86	87
150	90	92	88	89
165	90	93	90	90
180	91	94	91	91



METHACRYLONITRILE:

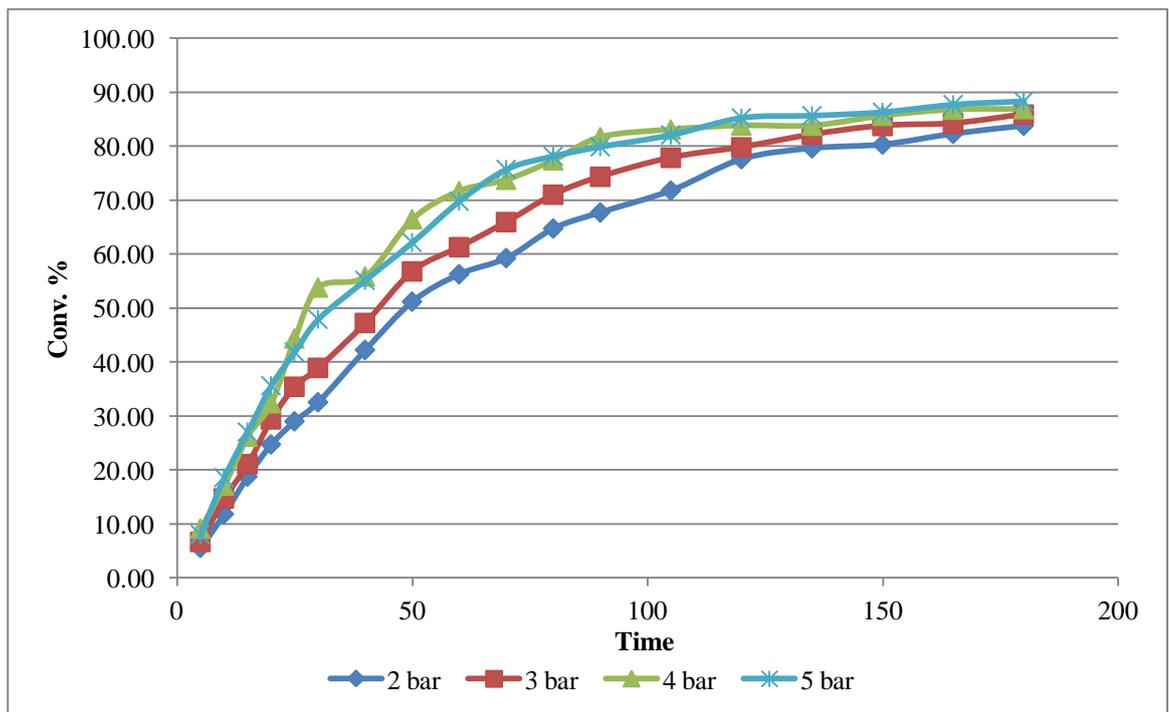
Temperature effect:

temp. Time	30 °C	40 °C	50 °C	60 °C	70 °C
	% Isobutyronitrile				
5	2	5	7	8	7
10	5	13	15	15	12
15	7	16	21	24	17
20	9	21	29	29	22
25	12	26	35	31	26
30	14	30	39	37	30
40	18	41	47	44	36
50	21	45	57	53	41
60	26	51	61	58	45
70	30	57	66	61	50
80	32	61	71	65	53
90	36	65	74	65	58
105	40	71	78	68	63
120	44	74	80	70	66
135	45	78	82	71	71
150	49	80	84	73	74
165	53	83	84	74	76
180	56	84	86	77	78



Pressure effect:

Time \ pressure	2 bar	3 bar	4 bar	5 bar
5	6	7	9	8
10	12	15	17	19
15	19	21	26	27
20	25	29	32	36
25	29	35	44	42
30	33	39	54	48
40	42	47	56	55
50	51	57	67	62
60	56	61	72	70
70	59	66	74	76
80	65	71	77	78
90	68	74	82	80
105	72	78	83	82
120	78	80	84	85
135	80	82	84	86
150	80	84	86	86
165	82	84	87	88
180	84	86	87	88



Concentration effect:

Time \ conc.	0.6 ml	0.8 ml	1 ml	1.2 ml
5	10	7	7	8
10	19	15	15	15
15	25	21	21	20
20	32	27	29	27
25	39	32	35	30
30	44	38	39	33
40	53	47	47	38
50	61	52	57	40
60	66	60	61	44
70	72	64	66	47
80	75	67	71	47
90	77	71	74	50
105	80	75	78	52
120	82	78	80	55
135	85	79	82	58
150	85	81	84	60
165	88	83	84	61
180	87	85	86	62

