



Akram, H., Monaghan, A., and Jackson, S. D. (2016) Comparison of C=C bond hydrogenation in C-4 unsaturated nitriles over Pt/alumina. *Industrial and Engineering Chemistry Research*, 55(7), pp. 1843-1848.

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Deposited on: 26 August 2016

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**A Comparison of C=C Bond Hydrogenation in C-4 unsaturated  
Nitriles over Pt/alumina.**

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## **Abstract.**

The hydrogenation of allyl cyanide (but-1-ene-4-nitrile, AC), trans- and cis-crotononitrile (E- and Z-but-2-ene nitrile, TCN and CCN), and methacrylonitrile (2-cyano-1-propene, MCN) were studied, both singly and competitively, over a Pt/alumina catalyst in the liquid phase. Each unsaturated nitrile only underwent C=C bond hydrogenation: no evidence was found for the formation of the saturated or unsaturated amine. The non-conjugated allyl cyanide was found to be the most reactive unsaturated nitrile. Activation energies for the hydrogenation of the C=C bond in AC and MCN were determined giving values of  $64 \pm 7 \text{ kJ.mol}^{-1}$  for AC and  $37 \pm 4 \text{ kJ.mol}^{-1}$  for MCN. The reaction was zero order for both nitriles. Competitive hydrogenations revealed that not only does allyl cyanide react preferentially over the other isomers but that it also inhibits the hydrogenation of the other isomers. When all four nitriles were simultaneously hydrogenated, inhibition effects were easily seen suggesting that in terms of strength of bonding to the surface an order of  $\text{AC} > \text{CCN} > \text{TCN} \sim \text{MN}$  can be generated.

Keywords: Hydrogenation, platinum, unsaturated nitriles

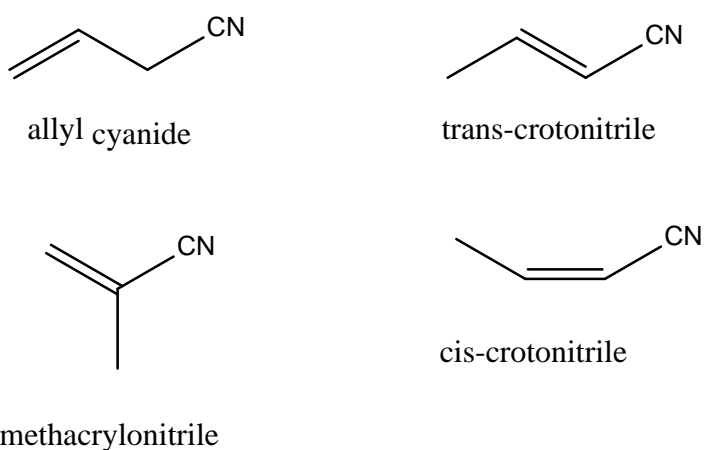
## Introduction

Selective hydrogenation is an important process in heterogeneous catalysis, with examples such as acetylene hydrogenation or acrolein hydrogenation. When more than one functional group is present there are many factors which can affect which functional group will be hydrogenated first. Hydrogenation of an unsaturated nitrile, may result in a saturated nitrile, a saturated amine and/or an unsaturated amine and properties such as functional group proximity or conjugation can affect which group is hydrogenated first. With a short chain unsaturated nitrile or conjugated system the C=C double bond should be hydrogenated preferably over the C≡N group from a thermodynamic point of view [1, 2]. In contrast when hydrogenating long chain nitriles or when the double bond is sterically hindered the hydrogenation of the double bond is slower than the CN triple bond [2]. Changing the surface character of the catalyst in bimetallic systems can also affect activity and selectivity in unsaturated nitrile hydrogenation [3]. Although the production of unsaturated amines is often the main interest in the hydrogenation of unsaturated nitriles, the selective hydrogenation of the C=C bond in nitrile-butadiene-rubber (NBR) is also of significant commercial importance [4]. In this application it is of paramount importance that the C=C bond is hydrogenated selectively over the nitrile as this ensures that oil resistance is maintained in the final material. Therefore catalysts that selectively hydrogenate the C=C bond in the presence of CN are also of interest.

Much of the recent work in the area of unsaturated nitrile hydrogenation has been related to the hydrogenation of pentenenitriles, especially cis-2-pentenenitrile and trans-3-pentenenitrile. Kukula and Koprivova [2] studied the hydrogenation of both species at high hydrogen pressures (> 80 bar) in the liquid-phase over a variety of catalysts such as Raney

nickel, Raney cobalt and versions modified with chromium. The primary product formed from the conjugated isomer (cis-2-pentenenitrile) was n-pentanenitrile, whereas the non-conjugated isomer, trans-3-pentenenitrile, produced the unsaturated amine trans-3-pentenamine. In a series of studies on cis-2-pentenenitrile and trans-3-pentenenitrile hydrogenation over Ni/alumina and Ni/silica catalysts [5 – 7] it was shown that there were five sites identifiable involved in hydrogenation and isomerisation and that the carbonaceous deposit played a significant role in specifying the chemistry.

The aim of this study was to investigate the hydrogenation of the C=C double bond in C-4 unsaturated nitriles over a Pt/alumina catalyst. The nitriles were allyl cyanide (AC, but-1-ene-4-nitrile), trans- and cis-crotonitrile (E- and Z-but-2-ene nitrile, TCN and CCN), and methacrylonitrile (MCN, 2-cyano-1-propene), Scheme 1. This combination allowed the comparison of both electronic and steric effects to be examined. CAN, CCN and TCN all make the same product, butyronitrile, while MCN generates iso-butyronitrile as its product.



**Scheme 1.** The four reactants involved in the hydrogenation study.

## Experimental

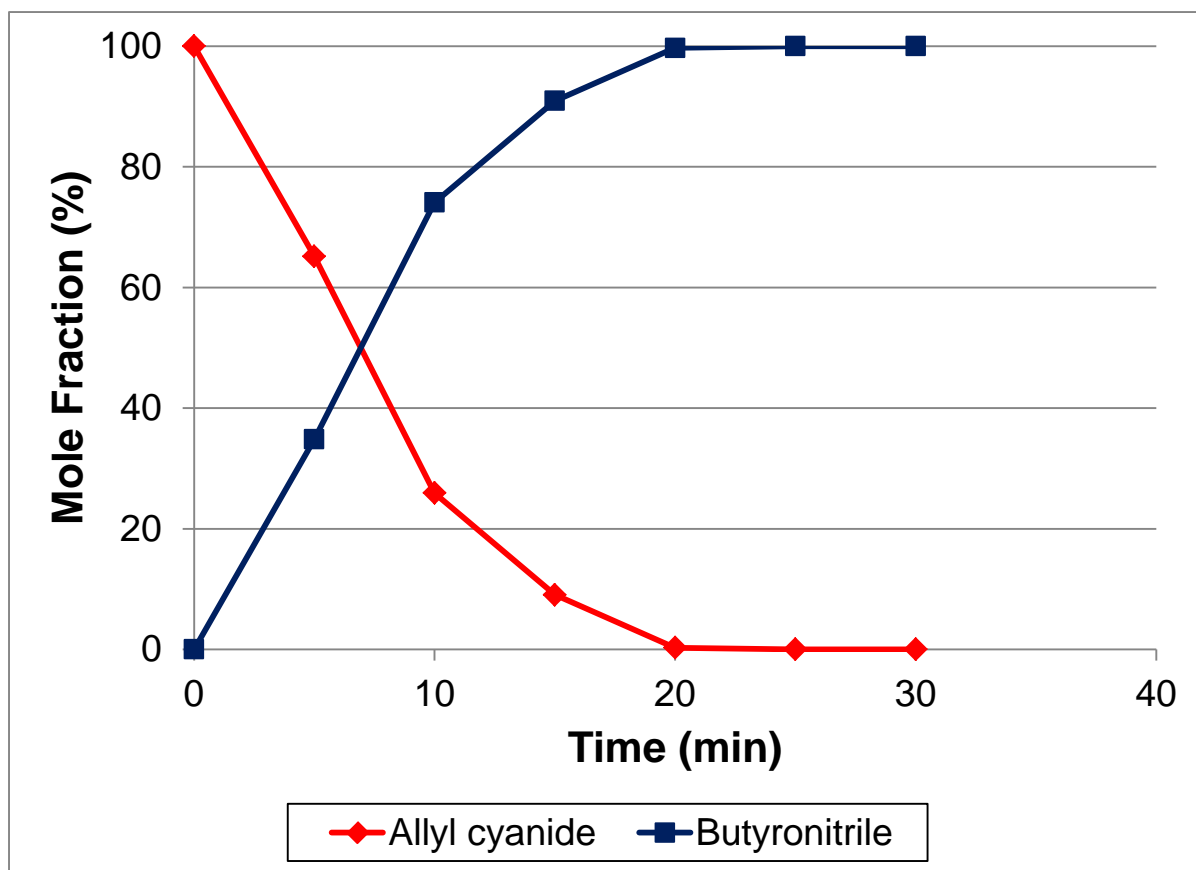
The catalyst used throughout this study was a 1 % Pt/ $\theta$ -alumina supplied by Johnson Matthey. The platinum dispersion, as measured by carbon monoxide chemisorption, was 56 %, while the catalyst had a BET surface area of  $119 \text{ m}^2 \cdot \text{g}^{-1}$ , a pore volume of  $0.49 \text{ cm}^3 \cdot \text{g}^{-1}$  and an average pore diameter of 11 nm. As the temperatures attainable within the reactor were not sufficiently high enough to guarantee full reduction of the catalyst *in situ* the catalyst was pre-reduced and stabilised before being used in the hydrogenation. The Pt/ $\text{Al}_2\text{O}_3$  catalyst was reduced by heating to 523 K at  $10 \text{ K} \cdot \text{min}^{-1}$  and holding the catalyst at this temperature for 2 h in flowing hydrogen ( $25 \text{ ml} \cdot \text{min}^{-1}$ ). The flow was then switched to argon and the catalyst cooled to room temperature. Once at room temperature the flow was changed to 2 % oxygen/argon ( $25 \text{ ml} \cdot \text{min}^{-1}$ ) for 0.5 h before the catalyst was discharged into the air. The re-reduction of the Pt/alumina was determined by temperature programmed reduction and was found to occur at temperatures of 333 K and above.

The reactor used for all the reactions was a 0.5L Buchi stirred autoclave equipped with a hydrogen-on-demand system and an oil jacket to control temperature. The catalyst (0.05g) was added to the reactor, followed by isopropyl alcohol (330 ml, IPA, Sigma 99.5 %). After heating the reactor to 333 K, the catalyst was re-reduced/reduced *in situ* by sparging the system with hydrogen for 30 min, whilst stirring the contents of the reactor at 300 rpm. Upon completion of the reduction the autoclave was set to the required reaction temperature. For the single system reactions the required volume of nitrile (1 ml, 0.012 mol unless otherwise specified, all Sigma > 98 %, crotononitrile had a *cis:trans* ratio of approximately 60:40) was

then injected into the reaction vessel with the stirrer switched off, followed by injection of 20ml of degassed IPA to ensure that all of the nitrile was flushed into the system. For the competitive reactions, the nitriles were added consecutively followed by 20 ml of degassed IPA. The autoclave was then stirred briefly (~30 s) at 1000 rpm , turned to 0 rpm and pressurised to approximately 0.4-0.5 barg of nitrogen, at which point the initial time zero sample was taken. The reactor vessel was depressurised then purged and pressurised with hydrogen to 1 barg after which the stirrer was set to a speed of 1000 rpm. Further samples were taken at regular intervals. The liquid samples obtained were then analysed by gas chromatography (GC). The GC used throughout this study was a Thermo Finnigan Focus GC equipped with an FID detector and a HP-1701 column (30m length x 0.25mm id, 1 micron film thickness). Standard tests (varying the stirring speed, using different catalyst weights) were undertaken to ensure the system was under kinetic control with no mass transfer limitations

## **Results.**

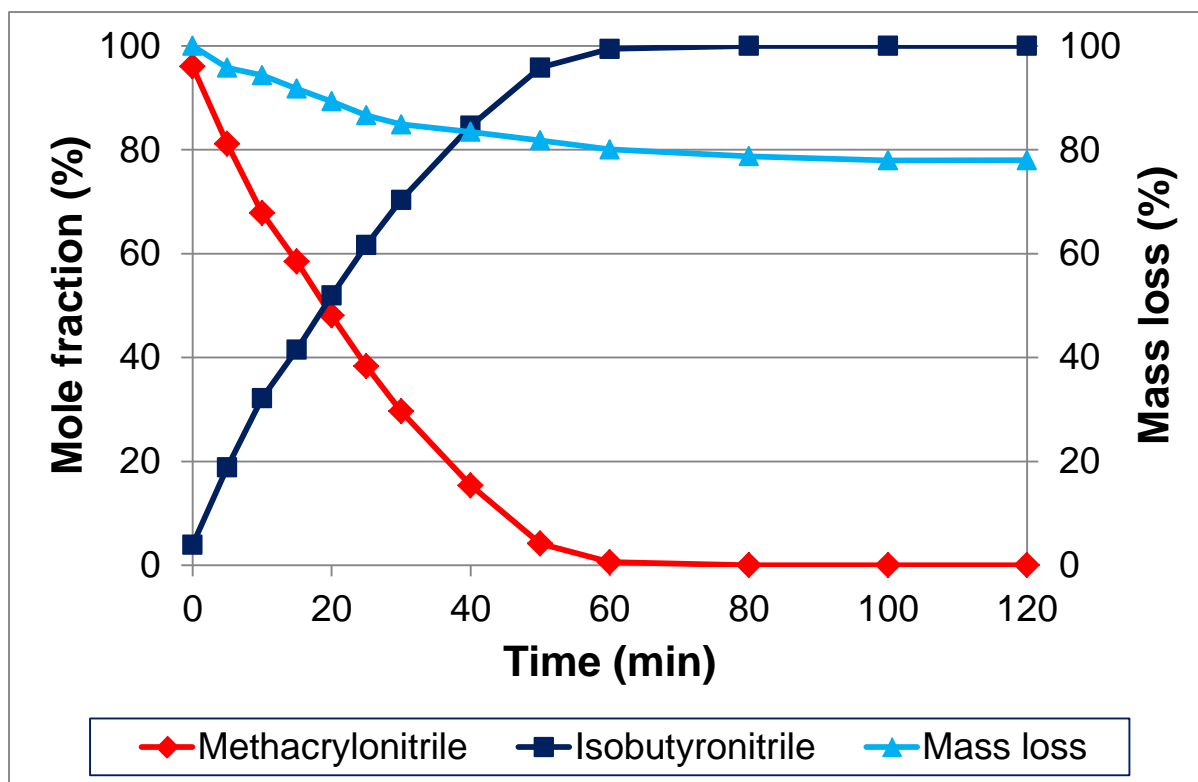
Analysis of the products from all of the liquid phase hydrogenations revealed only the saturated nitriles, no saturated amines or unsaturated amines were detected, i.e for allyl cyanide, cis-crotonitrile and trans-crotonitrile the sole product was butyronitrile, for methacrylonitrile the sole product was iso-butyronitrile. No isomerisation between the isomeric nitriles was observed under any conditions.



**Figure 1.** Reaction profile for allyl cyanide hydrogenation. Temperature 313 K, hydrogen pressure 1 barg, 50 mg of catalyst.

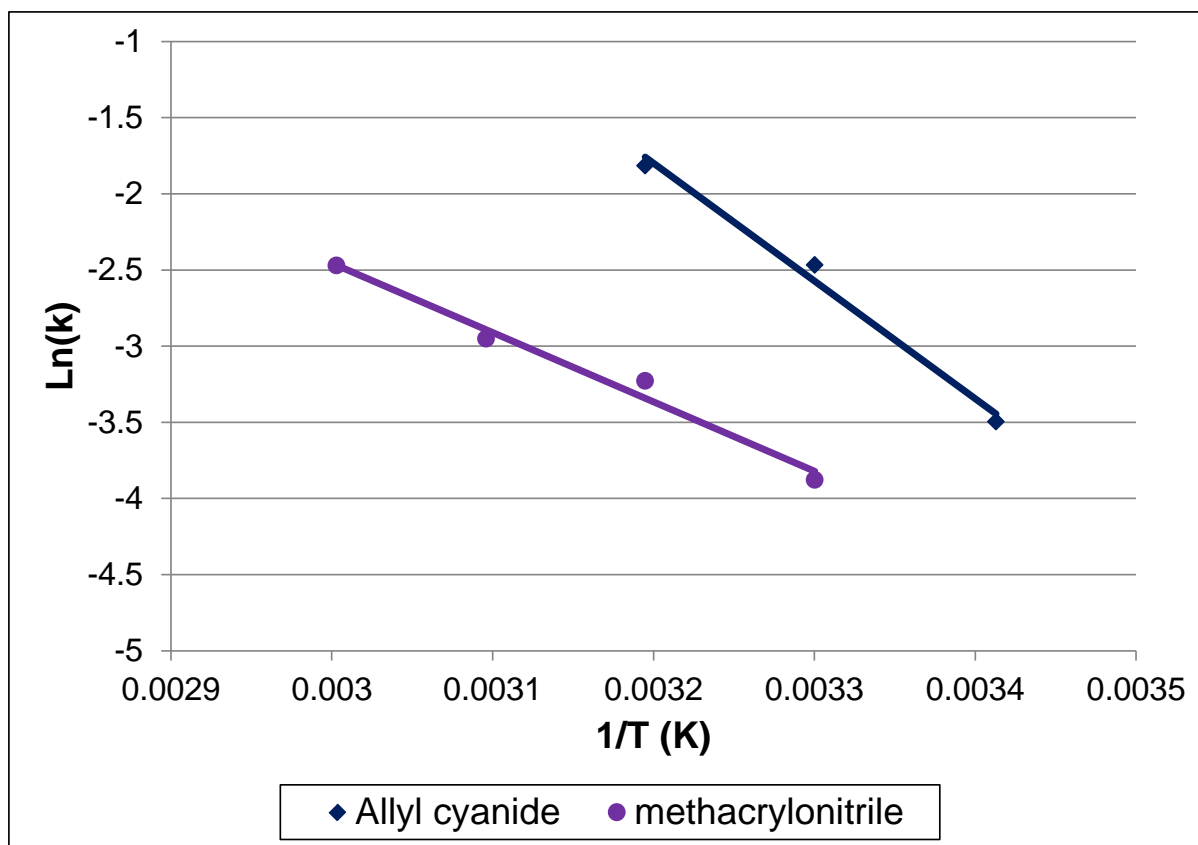
The reaction profile for allyl cyanide (AC) is shown in Figure 1. The mass balance was consistent across the whole reaction period at  $0.0107 \pm 0.0006$  moles. The loss of the reactant was analysed using first order kinetics ( $\ln[A_0]/\ln[A_t] = kt$ ) and a pseudo-first order rate constant of  $0.163 \pm 0.024 \text{ min}^{-1}$  determined. The reaction profile for methacrylonitrile (MCN) is shown in Figure 2. The mass balance during this reaction was such that there was an initial loss of reactant before reaching a stable state (Fig. 2). A pseudo-first order rate constant of  $0.040 \pm 0.001 \text{ min}^{-1}$  was calculated.





**Figure 2.** Reaction profile for methacrylonitrile hydrogenation. Temperature 313 K, hydrogen pressure 1 barg, 50 mg of catalyst.

The temperature of reaction was varied between 293 K and 333 K and activation energies were determined for both reactions. The activation energy plots are shown in Figure 3 and give values of  $64 \pm 7 \text{ kJ.mol}^{-1}$  for AC and  $37 \pm 4 \text{ kJ.mol}^{-1}$  for MCN.

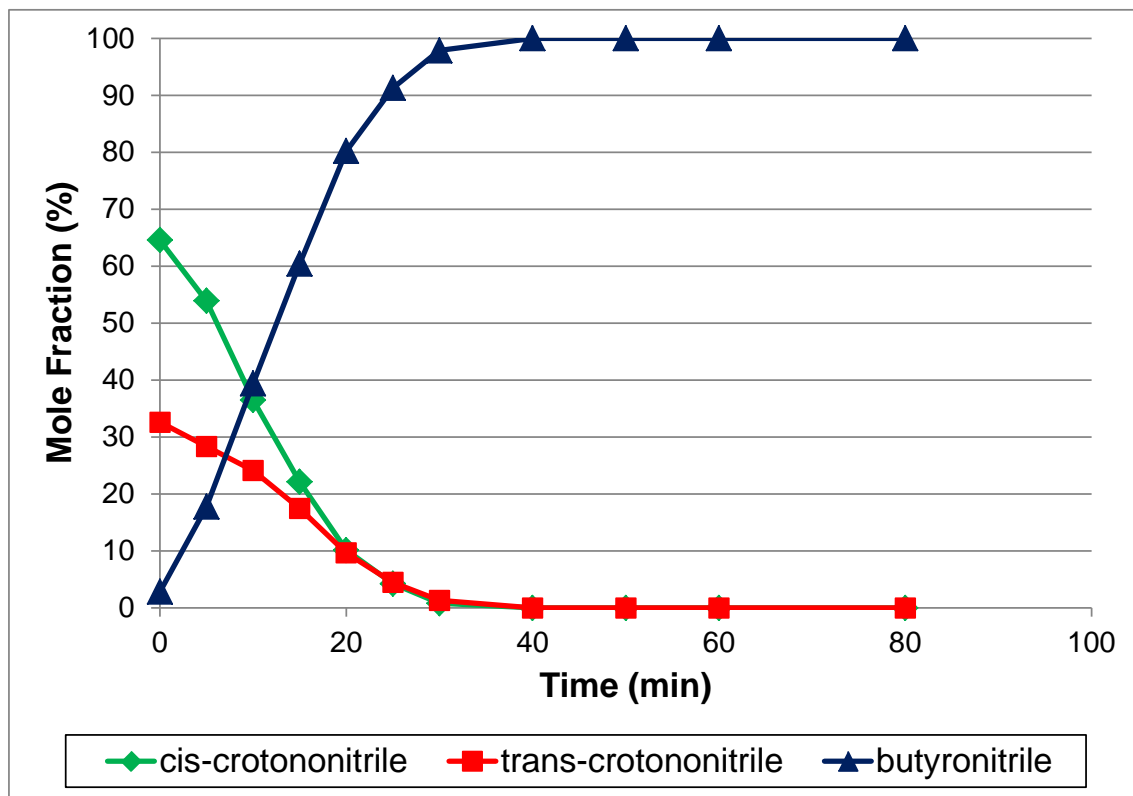


**Figure 3.** Activation energy plots for allyl cyanide and methacrylonitrile.

The reaction order for both nitriles was determined by changing the quantity of nitrile added between 0.006 mol and 0.024 mol. The order of reaction was approximately zero order for both nitriles.

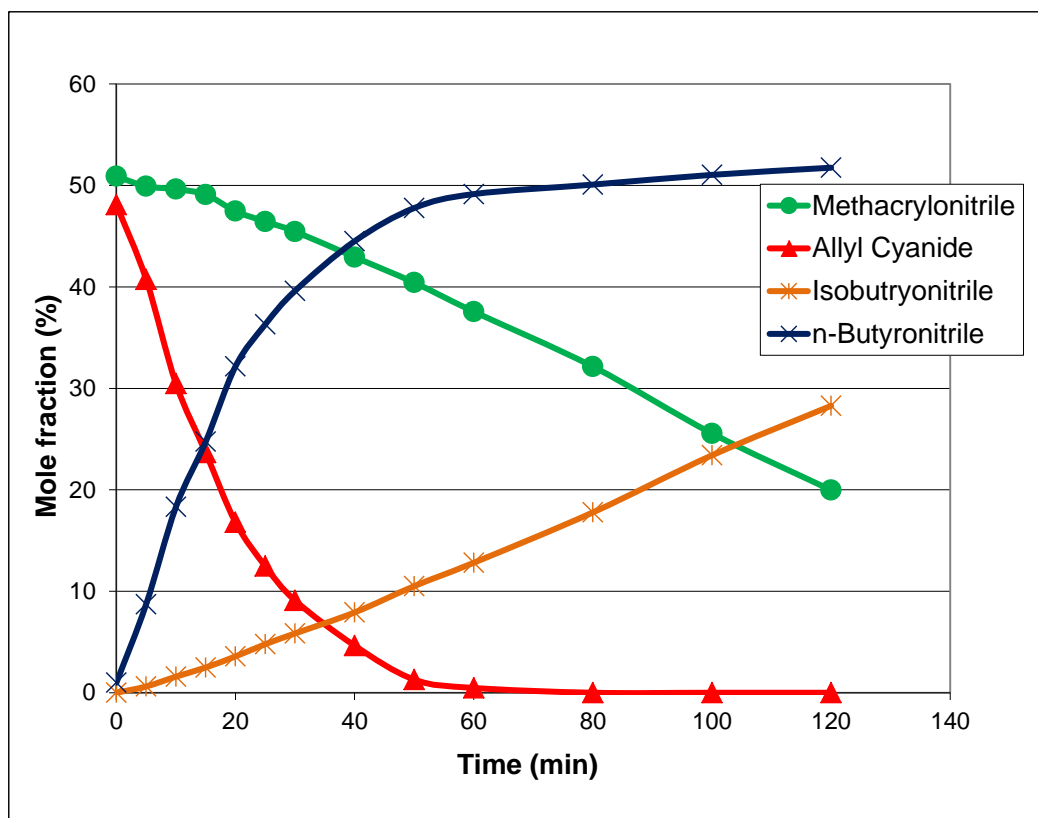
Five competitive hydrogenation reactions were investigated, TCN/CCN, AC/TCN/CCN, AC/MN, TCN/CCN/MCN and AC/TCN/CCN/MCN. The reaction profile for TCN/CCN is shown in Figure 4. The mass balance was consistent across the whole reaction at  $0.0109 \pm 0.0003$  moles. The other profiles are shown in Figures 5 – 8. Figure 5 shows the reaction profile for AC/MCN and it can be seen that the rate of hydrogenation of MCN to isobutyronitrile has been decreased from that for MCN in the absence of another species.

The mass balance showed no change over the course of the reaction with a value of  $0.0203 \pm 0.0009$  moles.

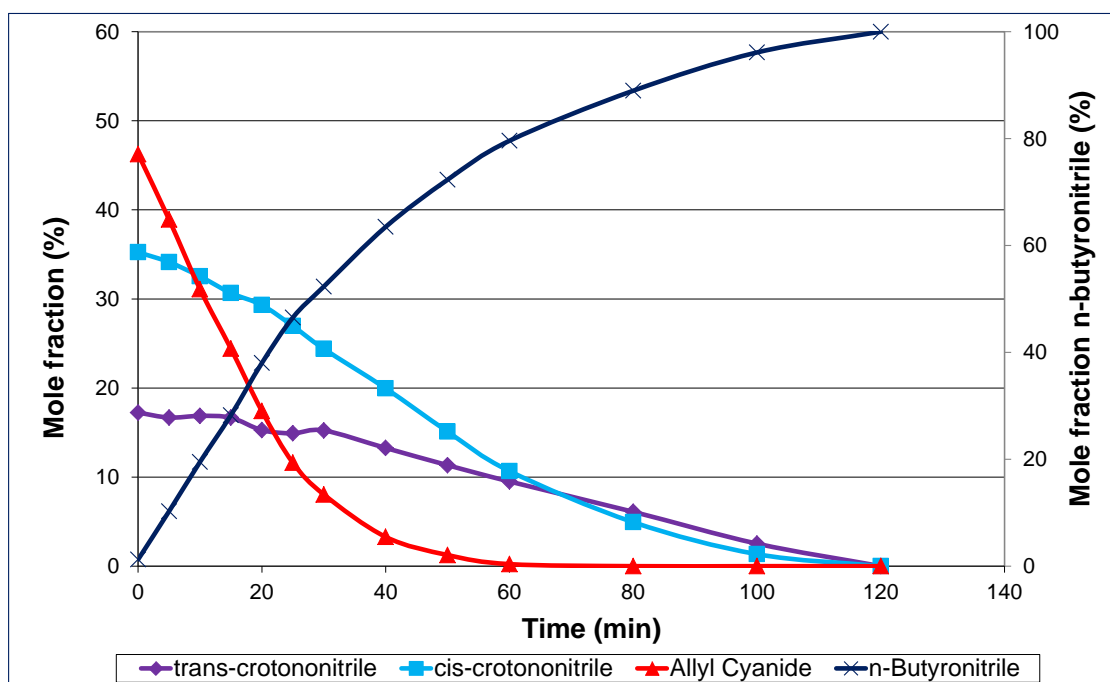


**Figure 4.** Competitive reaction between cis- and trans-crotononitrile. Temperature 313 K, hydrogen pressure 1 barg.

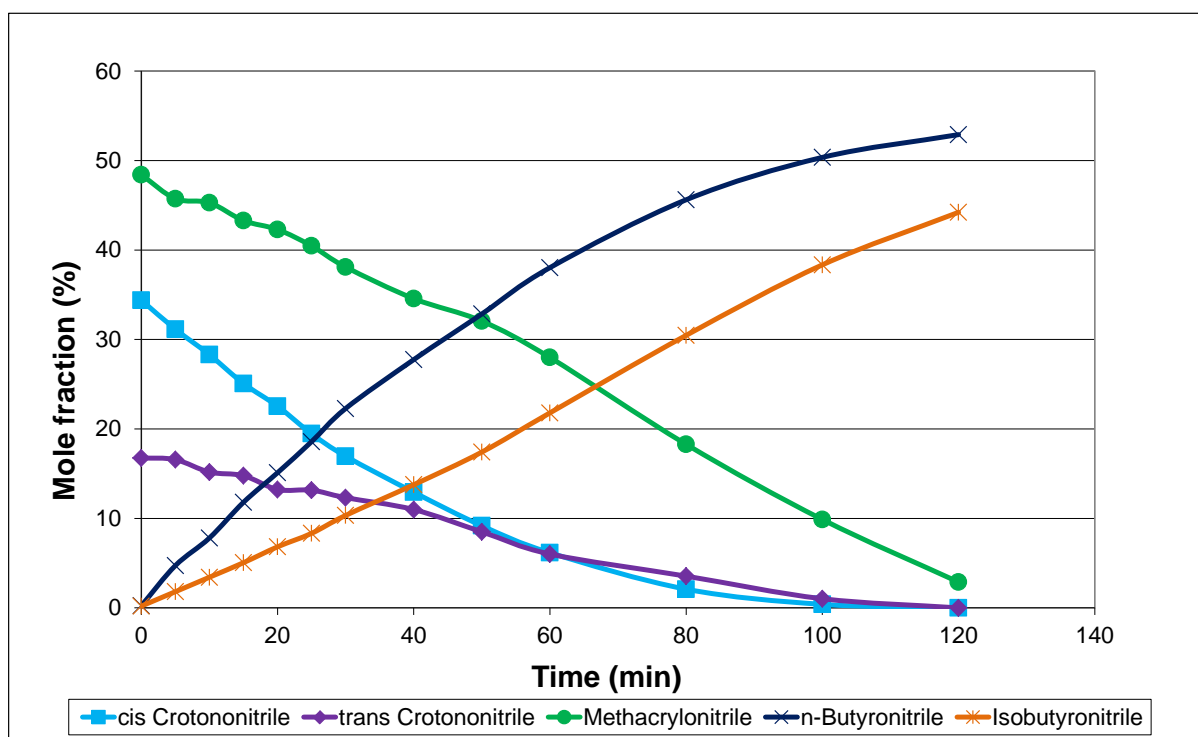
Figure 6 shows the reaction between AC/TCN/CCN. When compared with Figure 4 it is clear that the hydrogenation rates for TCN and CCN have decreased in the presence of AC. The mass balance was constant throughout the reaction at  $0.0216 \pm 0.0010$  moles.



**Figure 5.** Competitive reaction between allyl cyanide and methacrylonitrile. Temperature 313 K, hydrogen pressure 1 barg.



**Figure 6.** Competitive reaction between allyl cyanide and trans- and cis-crotononitrile. Temperature 313 K, hydrogen pressure 1 barg.



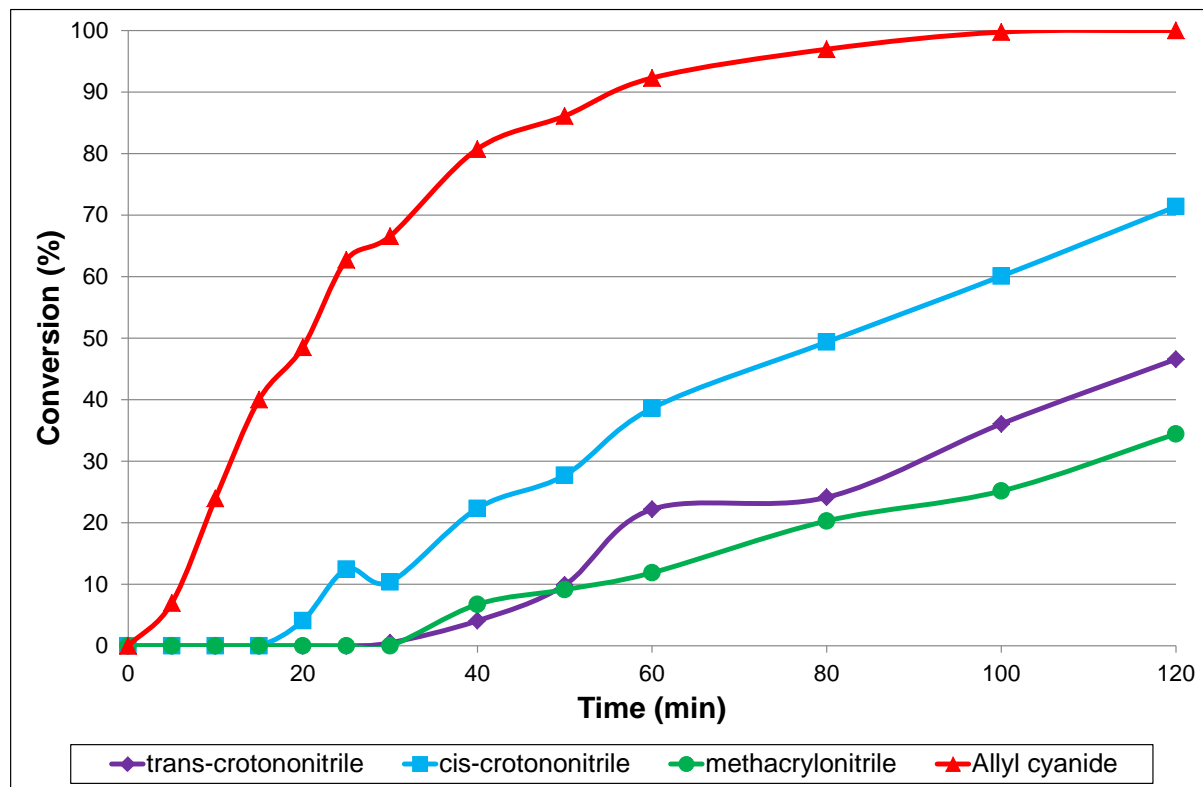
**Figure 7.** Competitive reaction between cis- and trans-crotononitrile and methacrylonitrile.

Temperature 313 K, hydrogen pressure 1 barg.

Figure 7 show the reaction profile for the MCN/TCN/CCN competitive reaction. All three reactants show depressed hydrogenation activity. The mass balance of the system was constant throughout the reaction with a value of  $0.0214 \pm 0.0021$  moles. In contrast to the single hydrogenation of MCN, the mass balance for MCN/isobutyronitrile was constant across the reaction.

Figure 8 shows the conversion for each component in the AC/TCN/CCN/MCN reaction. Clearly allyl cyanide inhibits the hydrogenation of methacrylonitrile and trans-crotononitrile and to a lesser extent cis-crotononitrile. The rate constants for the reactions, once they initiate, are reported in Table 1. However from table 1 we can see that even allyl cyanide is affected by the presence of a second component in the reaction. In the presence of

methacrylonitrile, the rate constant for allyl cyanide hydrogenation is only 37 % of that found when no second component is present.



**Figure 8.** Competitive reaction between allyl cyanide, cis- and trans-crotonitrile and methacrylonitrile. Temperature 313 K, hydrogen pressure 1 barg.

**Table 1.** Rate constants for the competitive reactions. Temperature 313 K, hydrogen pressure 1 barg.

Reactant(s)	Rate constants (min <sup>-1</sup> )			
	AC	CCN	TCN	MN
AC	0.163			
MCN				0.040
CCN/TCN		0.072	0.041	
AC/TCN/CCN	0.041	0.026	0.016	
AC/MCN	0.048			0.009
TCN/CCN/MCN		0.027	0.016	0.015
AC/TCN/CCN/MCN	0.045	0.012	0.007	0.004

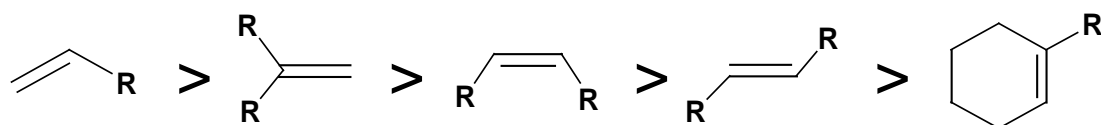
## Discussion

When hydrogenated over the Pt/alumina catalyst each unsaturated nitrile only undergoes C=C bond hydrogenation. There is no evidence for the formation of the amine, either saturated or unsaturated. In previous studies using *cis*-2-pentenenitrile as the reactant, the saturated amine product was observed over a Ni/alumina catalyst [5, 7]. In those studies it was shown that there was a site on the alumina, which could produce the saturated amine [5, 7]. As it is the same alumina used in this study we must ask, why was no saturated amine generated?

However it should be noted that the *cis*-2-pentenenitrile studies [5, 7] were conducted in the gas phase and indeed when *cis*-2-pentenenitrile is passed over this Pt/alumina catalyst at 373 K in the gas phase the saturated amine is produced initially in high yield [8]. Hence the

absence of the saturated amine for the C4 nitriles may be due to two, not mutually exclusive, causes. The temperature used in this study is much reduced from the gas phase study and the rate reduction may not allow for any significant amine production, especially if a high activation energy was extant. Secondly the solvent may interfere with the site on the alumina. The site was postulated to be a hydroxyl [7] and these may be replaced by the isopropoxy ion from the IPA solvent. A study over Raney Nickel of the hydrogenation of allyl cyanide and crotononitrile [9] at ~308 K in the liquid phase also found no evidence for the formation of the amine and attributed this to the low temperature.

The rate of hydrogenation of the C=C bond in AC is much greater than that of MCN. In terms of steric hindrance we may expect an ordering which would follow the pattern set out in Scheme 2:



**Scheme 2.** Order of reactivity of isolated C=C bonds

This would give an order of AC > MN, which is similar to that found experimentally except there is also the effect of conjugation; it would be expected that the conjugated C=C bond would be more reactive [2, 7] but it would appear that steric effects are the dominant factor rather than any effect of conjugation. This is in contrast to that found when cis-2-pentenenitrile and trans-3-pentenenitrile were hydrogenated over Raney Nickel, [2] where the conjugated cis-2-pentenenitrile reacted faster than the non-conjugated trans-3-pentenenitrile to give the saturated nitrile. It is also in contrast with a study of conjugated and non-conjugated alkenyl benzenes [10] where the conjugated cis-isomer was the most reactive.



Nevertheless it is in agreement with the study by Delmon and co-workers [9] who found the non-conjugated allyl cyanide reacted faster than crotononitrile.

Both AC and MCN displayed zero order kinetics in terms of organic and it would be expected that the order of reaction in hydrogen would be first order. The activation energies are interesting in that the activation energy for allyl cyanide was significantly higher than that of methacrylonitrile. The activation energy for AC ( $64 \pm 7 \text{ kJ.mol}^{-1}$ ) is a typical value for an isolated C=C double bond, e.g ethene hydrogenation over a Pt/alumina catalyst has an activation energy of  $63 \text{ kJ.mol}^{-1}$  [11] while propene has a value of  $67 \text{ kJ.mol}^{-1}$  [12]. The activation energy of  $37 \pm 4 \text{ kJ.mol}^{-1}$  for MCN is similar to that found for a conjugated C=C bond, e.g. in the case of 1,3-butadiene over Pt/alumina an activation energy of  $39 \pm 5 \text{ kJ.mol}^{-1}$  [13] was calculated. This behaviour is in keeping with the results of Bartok and co-workers [14], who found that the hydrogenation behaviour of the C=C bond in 3-penten-2-one over different metals was predictable from alkene hydrogenation. The loss of mass in the MCN hydrogenation is typical of unsaturated nitrile hydrogenation, indeed it is more surprising that the none of the other experiments showed any evidence of mass loss. Studies of cis-2-pentenenitrile and trans-3-pentenenitrile [6, 7] have shown significant carbon laydown, which affected reaction selectivity as well as activity.

In the competitive hydrogenation of cis- and trans-crotononitrile it is clear that the cis-crotononitrile is much more reactive than the trans-isomer. This behaviour has been seen many times with different cis- trans-isomers, e.g. with pentenes [15, 16] an order of reactivity of cis-2-pentene > 1-pentene > trans-2-pentene was observed, while a similar pattern was observed for cis- and trans-2-hexene and cis- and trans-3-heptene [17]. This is related to the thermodynamic stability of the trans-isomers.

The competitive hydrogenations show quite clearly that not only does allyl cyanide react faster than the other isomers (Table 1) but that it also inhibits the hydrogenation of the other isomers (Figs. 1, 5, 6 and 8). When allyl cyanide and crotononitrile and co-hydrogenated there is an initial delay of around 15 min before the trans-crotononitrile starts to hydrogenate by which time around 40 % of the allyl cyanide has been converted. A similar effect is seen with the AC/MCN competitive react (Fig. 5). When all four nitriles are simultaneously hydrogenated, the inhibition effects are easily seen (Fig. 8). This inhibition suggests that in terms of strength of bonding to the surface an order of  $AC > CCN > TCN \sim MN$  can be generated, which follows the order of reactivity. That MCN should have the lowest reactivity is not surprising: it can be shown that the methyl group will sterically inhibit adsorption of the C=C bond and so reduce strength of bonding and activity. To understand the difference between AC, CCN and TCN it is informative to consider a study examining trans-3-pentenitrile and cis-2-pentenitrile [5, 7]. Studies using deuterium [7] in the hydrogenation of cis-2-pentenitrile revealed that the deuterium was present in every position of the product pentanenitrile. This was interpreted by showing that adsorption of both C=C and CN functions allowed the formation of two  $\pi$ -allyl structures. With the C-4 unsaturated nitriles formation of a  $\pi$ -allyl intermediate would result in a common species between cis-, trans-crotononitrile and allyl cyanide, if this were to be the case then it would be expected that all three isomers would show similar reactivity. Indeed spectroscopic studies of acetonitrile adsorption on Pt [18, 19] reveal an end-on bonding, which would be in keeping with the proposal that the C=C bond in AC is not directly bonded to the surface [9] and that the hydrogenation occurs via cyclic intermediate. However for the conjugated systems the proposal is that both functionalities are bonded to the surface [7, 9].

We could find no literature on competitive hydrogenation of unsaturated nitriles, Schäringer *et al.* [20] 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. However the reactivity of both nitriles was reduced [20]. Much more research has been conducted on conjugated aldehydes and theoretical studies [21] suggest that the adsorption is crystal face sensitive, something which has been shown for nitrile hydrogenation over Pt catalysts [18]. Control of the selectivity in conjugated aldehydes has been investigated and a theoretical study into the hydrogenation over Pt(III) of acrolein, which yields the saturated aldehyde and prenal (methylbutenal), which yields the unsaturated alcohol [22]. The conclusion was that the selectivity was determined by the desorption step although hydrogenation of the C=O bond was favoured on the surface to yield propenol, desorption was easier for the product arising from hydrogenation of the C=C bond (propanal).

The rate constants for all the competitive hydrogenations show a reduction relative to the single hydrogenation (Table 1). The rate constant for AC hydrogenation in presence of competing nitriles is approximately  $0.045 \text{ min}^{-1}$  which represents around  $\frac{1}{4}$  of the value calculated when AC is hydrogenated in the absence of competing species. Similarly with TCN and CCN, the rate constants found when AC and MCN are the competing species, are  $\sim 0.017$  and  $\sim 0.026 \text{ min}^{-1}$  respectively. No such trend is found with MCN. From the above discussion allyl cyanide is the most strongly bound species and inhibits the adsorption of any of the other nitriles, therefore we must question why does rate of ally cyanide hydrogenation reduce? One option is due to a reduction in the hydrogen flux. The reaction can be expected to have a positive order in hydrogen so any drop in hydrogen surface concentration would have a significant effect on the rate of hydrogenation. A reduction in the amount of adsorbed

allyl cyanide could also potentially reduce the rate. However when the competitive reaction was repeated at various concentrations a zero order of reaction was observed for AC, indicating that there was high surface coverage even when the concentration in solution was halved. This would tend to suggest that the surface coverage of AC is not controlling the reduction in rate. All of the nitriles will be more strongly bound to the platinum than hydrogen [23] hence the hydrogen atom flux at the surface can be significantly reduced leading to a rate will decrease. However this implies that there are adsorption sites where nitriles may adsorb but not react. This is plausible as there will be a range of adsorption sites and energetics on the surface.

## **Conclusions**

In this study we have examined the hydrogenation of allyl cyanide and methacrylonitrile and have shown that hydrogenation of the isolated C=C bond has the same activation energy as a hydrocarbon C=C and that hydrogenation of the conjugated C=C bond has the same activation energy as conjugated bond in a hydrocarbon. Therefore we can use our understanding of these systems to aid our understanding of the unsaturated nitrile systems. The competitive hydrogenation of unsaturated nitriles has been studied and it has been shown that allyl cyanide hydrogenates preferentially over cis- and trans-crotonitrile and methacrylonitrile, to the extent that allyl cyanide inhibits hydrogenation of the other species until ~50 % of the allyl cyanide has been converted. In a competitive system cis-crotonitrile hydrogenates preferentially over the trans-isomer, which is consistent with alkene systems. Methacrylonitrile hydrogenation is inhibited by the presence of cis- and trans-crotonitrile.

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