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ScienceDirect

Catalysis Today 128 (2007) 47–51

CATALYSIS TODAY

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Hydrogenation of unsaturated hydrocarbons—40 years on: Hydrogenation of 1,3-pentadiene over Pd/alumina

S. David Jackson *, Andrew Monaghan

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

Abstract

The hydrogenation of 1,4-pentadiene, *E*-1,3-pentadiene, and a *Z*/*E*-1,3-pentadiene mix have been studied over a Pd/alumina catalyst in the liquid phase at 313 K. 1,4-Pentadiene was found to react in a manner similar to 1-pentene. However, *E*-1,3-pentadiene caused rapid deactivation of the catalyst. When a *Z*/*E*-1,3-pentadiene mixture was hydrogenated no such deactivation was observed and the initial rate of *E*-1,3-pentadiene hydrogenation was reduced. It is proposed that the adsorbed *Z*-1,3-pentadiene disrupts π-stacking of the *E*-isomer. The pentene isomer selectivity indicated that 3,4-addition was favoured, which indicated that the internal double bond was more reactive than the terminal double bond. The reaction of 1,4-pentadiene in competition with 2-pentyne resulted in an increased rate of reaction for both reactants. Whereas the reaction of *Z*/*E*-1,3-pentadiene in competition with 2-pentyne or 1-pentyne resulted in a decreased rate of reaction for both reactants. In this case the alkene isomer selectivity could be modelled by simple averaging of the individual selectivities.

Keywords: Hydrogenation; Pentadiene; Palladium; Pentyne

1. Introduction

Around 40 years ago, in the late 1960s, research into alkyne and alkene hydrogenation over precious metal catalysts was in its heyday. Even though Sabatier had received a Nobel Prize in Chemistry in 1912 for hydrogenation of organic compounds over finely divided metals [1] and others had continued the work, it was the studies of Bond et al. [2–7] in the mid to late 1960s that really defined hydrogenation of light alkynes and alkenes up to the present day. Indeed so successful and encompassing were these studies that research into such hydrogenation was almost moribund by the end of the 1970s – hydrogenation was no longer sexy – it had become a mature area in which everything, including the kinetics and mechanism, was pretty much understood. However, for those researchers who remained active in the area, including those named above, it was clear that everything was not understood and although our ability to produce highly active and selective hydrogenation catalysts was self evident, it was not through a fundamental understanding of the catalysts or the surface processes. In the intervening years the volume of publications in this area has significantly decreased but the need for fundamental understanding of inherently complex systems has not diminished.

In this paper we have examined the hydrogenation of pentadienes over a palladium catalyst and examined their reaction when other reactants, namely alkynes, are present. Many of the early studies, quite rightly, studied the hydrogenation of single components, however as our knowledge has increased it is important that we also consider competitive systems, as it is rare for single component hydrogenation in practical application. Also, in terms of strength of adsorption, it has been suggested that alkynes should be stronger than alkadienes and hence they should inhibit alkadiene hydrogenation. However, as has been shown in the case of alkenes hydrogenated in competition with alkynes [8] the older simplistic interpretations do not describe a competitive reaction very well. The results show that in the single component systems there is a clear linkage between the early interpretations and the most up-to-date understanding of unsaturated carbon–carbon hydrogenation.

2. Experimental

The catalyst used throughout this study was a 1% (w/w) palladium on alumina supplied by Johnson Matthey. The

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* Corresponding author.
E-mail address: sdj@chem.gla.ac.uk (S.D. Jackson).

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doi:10.1016/j.cattod.2007.04.013

support consisted of θ-alumina trilobes (S.A. ~100 $m^2 g^{-1}$) and the catalyst was sized to <250 μm for all catalytic studies. 1-Pentyne, 2-pentyne, *E*-1,3-pentadiene, 1,4-pentadiene and 1,3-pentadiene (all Aldrich >99%) were used without further purification. No significant impurities were detected by GC. 1,3-Pentadiene, unless specifically stated as *E*-1,3-pentadiene, was a 2:1 mixture of *E*-1,3-pentadiene:*Z*-1,3-pentadiene. The gases (BOC, >99.99%) were used as received.

The reaction was carried out in a 0.5 l Buchi stirred autoclave equipped with an oil jacket and a hydrogen-on-demand delivery system. 0.05 g of 1% Pd/Al_2O_3 was added to 330 ml of degassed solvent, hexane. Reduction of the catalyst was performed *in situ* by sparging the system with H_2 (300 $cm^3 min^{-1}$) for 30 min at 313 K while stirring the contents of the autoclave at 800 rpm. After reduction, the autoclave was adjusted to the appropriate reaction temperature of between 298 and 333 K under a nitrogen atmosphere. For pentadiene studies, 1 ml was injected into an unstirred solution, followed by 20 ml of degassed hexane to ensure that all the reactant was washed into the reactor. For the competitive reactions, 1 ml of each reactant was added prior to solvent injection. The autoclave was then mixed briefly at a stirrer speed of 800 rpm and pressurised to 1 bar with nitrogen and a sample was taken. The vessel was then depressurised and then pressurised with hydrogen to 2 bar. Following this the stirrer was set to a speed of 1000 rpm and samples were taken via a sample valve at defined time intervals. The liquid samples were analysed by gas chromatography on an Agilent 6890 Series. The column used was a 50 m Chrompack CP-Al_2O_3/Na_2SO_4. Standard checks were undertaken to confirm that the system was not under mass transport control.

3. Results

3.1. Hydrogenation of pentadienes

The reaction profile for *E*-1,3-pentadiene is shown in Fig. 1, where it can be seen that the major product was *E*-2-pentene apparently suggesting the selective reduction of the terminal alkenoic bond. Initially the reaction was fast with a first order rate constant of 0.028 min^{-1}. However, there was rapid deactivation after the first 10 min such that even after 2 h the reaction had barely reached 50% conversion. The reaction profile for 1,4-pentadiene is shown in Fig. 2. The initial rate constant was 0.016 min^{-1}. For this reaction three components all showed selectivities around 30%, 1-pentene, *E*-2-pentene and pentane. The reaction profile of the hydrogenation of 1,3-pentadiene is shown in Fig. 3. The initial rate constants were calculated as 0.014 min^{-1} for the *Z*-isomer and 0.016 min^{-1} for the *E*-isomer. The main products were *E*-2-pentene and pentane. No evidence was found for isomerisation between *Z* and *E*-1,3-pentadiene indicating that the isomerisation seen for the mono-alkene occurred either during or subsequent to the hydrogenation process. The selectivities obtained at 50% conversion for each of the above systems is reported in Table 1.

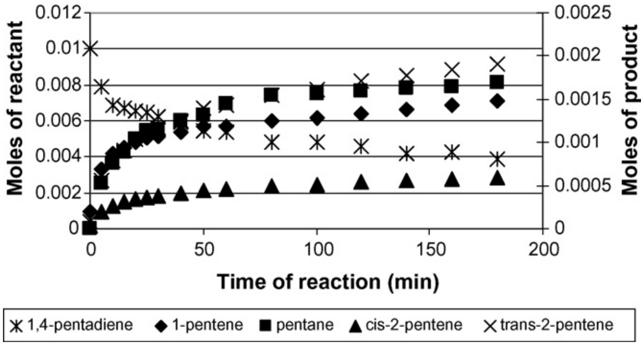


Fig. 2. Reaction profile of hydrogenation of 1,4-pentadiene.

3.2. Competitive hydrogenation

The effect of adding alkynes, 1-pentyne, and 2-pentyne, into the alkadiene reaction mix was investigated. The first order rate constants are reported in Table 2 along with those of the materials in absence of the competitor species. Both alkynes reduced the rate of reaction of 1,3-pentadiene and vice versa, however the rate of hydrogenation for 2-pentyne when reacted with 1,4-pentadiene increased and vice versa. The alkene isomer pattern was also analysed and the comparison is shown in Table 3. The model data were calculated using data from the individual hydrogenations at conversions equivalent to each component in the competitive reaction.

4. Discussion

The reaction scheme for the hydrogenation of pentadienes is shown in Scheme 1. It would appear from Scheme 1 that 1,4-pentadiene can only produce 1-pentene, all other isomers formed by isomerisation. Similarly *E*-1,3-pentadiene can only

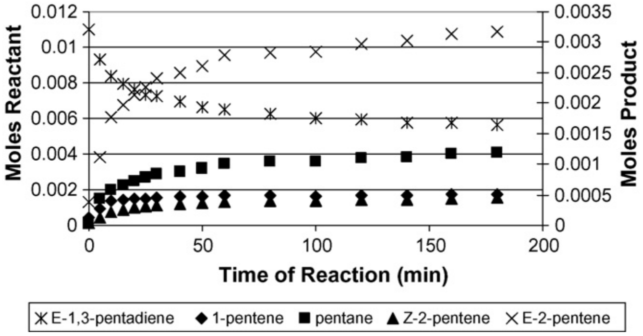


Fig. 1. Reaction profile of hydrogenation of *E*-1,3-pentadiene.

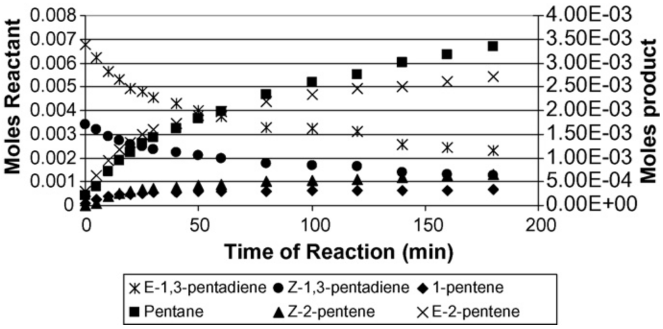


Fig. 3. Reaction profile of hydrogenation of a *Z*/*E*-1,3-pentadiene mix.

Table 1
Reaction selectivities at 50% conversion

Reactant	Time taken to reach 50% conversion (min)	Selectivity (%)			
		1-Pentene	*Z*-2-Pentene	*E*-2-Pentene	Pentane
1,3-Pentadiene	80	6	9	41	44
		11	16	73	
E-1,3-Pentadiene	180	10	8	60	22
		13	10	77	
1,4-Pentadiene	80	26	10	32	32
		38	15	47	

form *E*-2-pentene and 1-pentene, and *Z*-1,3-pentadiene can only form *Z*-2-pentene and 1-pentene. However, this view is deceptive, when the adsorbed states are considered, how a hydrogen atom adds to the adsorbed molecule influences the mono-ene product distribution (Scheme 2 [9]). Hydrogen may add to adsorb 1,3-pentadiene in three ways, 1,2-addition, 1,4-addition and 3,4-addition. The extent to which hydrogen adds in each of these modes has a significant effect on the distribution of pentene isomers.

Hydrogenation of 1,4-pentadiene is the simplest in that it is a non-conjugated diene where the primary product is 1-pentene with other isomers formed by isomerisation. At ~2% conversion the selectivity within the three mono-alkenes is 63% 1-pentene, 9% *Z*-2-pentene and 28% *E*-2-pentene. This high level of 1-pentene at low conversions confirms 1-pentene as the primary product. However, as time and conversion increase, the ratio rapidly moves to favour *E*-2-pentene (the thermodynamically most stable mono-ene isomer), e.g. within 5 min the conversion is 20% with an isomer ratio of 48% 1-pentene, 13% *Z*-2-pentene and 39% *E*-2-pentene. This type of behaviour is similar to that seen with 1,5-hexadiene and 1,7-octadiene [10]. No isomerisation of 1,4-pentadiene to *Z*- or *E*-1,3-pentadiene was detected.

According to Scheme 2 the hydrogenation of *E*-1,3-pentadiene can produce 1-pentene, *Z*-2-pentene and *E*-2-pentene as primary products and this is borne out by the isomer ratio at ~5% conversion of 23% 1-pentene, 5% *Z*-2-pentene and 71% *E*-2-pentene. This product distribution is significantly different from that found in a recent FTIR study of gas phase hydrogenation of *E*-1,3-pentadiene [11] where only the *E*-2-pentene isomer was detected. The high 1-pentene yield confirms that a significant amount of 3,4-addition must occur, given that 1-pentene is the least thermodynamically stable isomer and would only be expected to be present at thermodynamic equilibrium at around the 1% level. Indeed hydrogenation of conformation (a) in Scheme 2 can give rise to a 3:1 *E*-2-pentene:1-pentene ratio [10] suggesting that the contribution from other conformations is negligible. Hence,

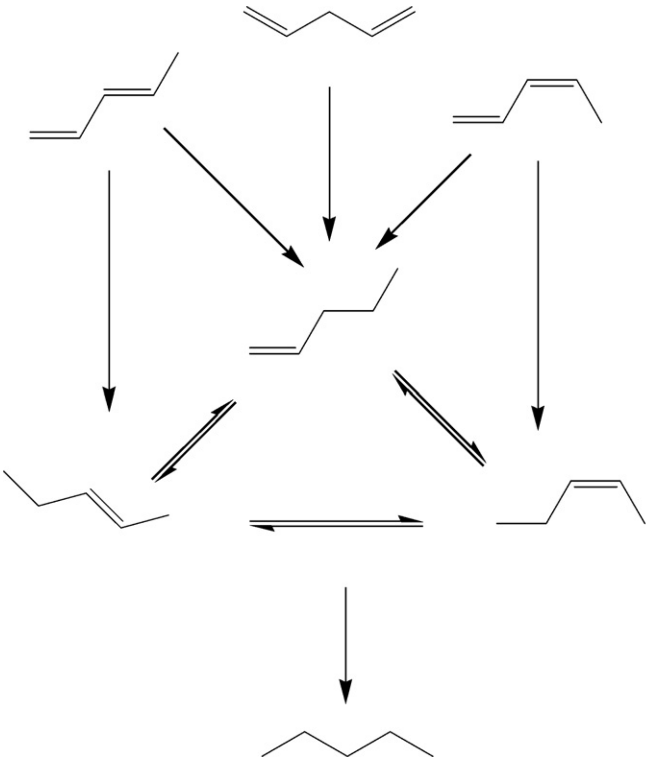
Table 2
Effect of alkyne on pentadiene hydrogenation

Reaction mix	Rate constant ($\times 10^{-3}$ min^{-1})				
	Z-1,3-PD	*E*-1,3-PD	1,4-PD	1-Pentyne	2-Pentyne
1,3-PD/1-pentyne	8	8		10	
1,3-PD/2-pentyne	3	3			3
1,4-PD/2-pentyne			36		43
1-Pentyne				33	
2-Pentyne					16
1,3-PD	14	16			
1,4-PD			16		

Table 3
Alkene isomer pattern

Reaction mix	1-Pentene (%)	*Z*-2-pentene (%)	*E*-2-pentene (%)
1,3-PD/1-pentyne	37	14	49
Model	42	12	46
1,3-PD/2-pentyne	11	42	47
Model	8	41	51
1,4-PD/2-pentyne	24	56	20
Model	22	39	39

Model values were generated by averaging the individual selectivities at the equivalent conversions.



Scheme 1.

although different from the FTIR study [11], the product distribution in the current study is in agreement with other catalytic literature [9,10] and suggests that the methyl group must increase the reactivity of the adjacent double bond to overcome any negative bias through increased steric crowding. The catalyst is rapidly deactivated, loss of activity occurring when conversion reaches ~25% with an alkene selectivity of 80%, 75% of which is *E*-2-pentene. The hydrogenation of *E*-2-pentene is also known to be slow [8] hence we may expect that the final hydrogenation step to pentane would be retarded but in fact all reactions are inhibited, hydrogenation of the diene, hydrogenation of mono-enes and isomerisation. Mass balance shows a systematic loss of material to the catalyst surface (Fig. 4). By the end of the run the ratio of C-5 molecules retained by the catalyst to Pd atoms in the system is approximately 100:1. Even after the first 10 min the ratio is over 50:1. To achieve such a high ratio it is likely that the adsorbed species polymerises. In the final 40 min the conversion over this period is minimal with the mass loss contributing significantly to the small change in conversion. This deactivation by ‘‘*E*’’ hydrocarbons does not require a conjugated system as *E*-2-pentene hydrogenation is similarly deactivated [8].

When a 2:1 *E*-1,3-pentadiene:*Z*-1,3-pentadiene mixture is hydrogenated the initial rate constant for the *E*-1,3-pentadiene is approximately half of that found with *E*-2-pentadiene alone (0.016 min^{-1} versus 0.028 min^{-1}), while the value for *Z*-1,3-pentadiene is 0.014 min^{-1}. Hence the addition of *Z*-1,3-pentadiene to *E*-1,3-pentadiene is to reduce the initial rate and indeed after 5 min the conversion of *E*-1,3-pentadiene is 8% in presence of *Z*-1,3-pentadiene compared to 16% in a solo reaction. It has been suggested in literature [11] that in a gas phase system *Z*-1,3,-pentadiene does not hydrogenate but rapidly isomerises to *E*-1,3-pentadiene, which is then hydrogenated. This was proposed to explain the absence of 1-pentene and *Z*-2-pentene with *E*-2-pentene being the sole intermediate product [11]. Part of the argument for this proposal was that hydrogenation of *Z*-1,3-pentadiene should give *Z*-2-pentene, however as can be seen from Scheme 2 both isomers of 1,3-pentadiene can produce all three pentene isomers. Indeed the mono-ene isomer ratio observed at less than 3% conversion of the *Z*/*E*-1,3-pentadiene mix is 12% 1-pentene, 2% *Z*-2-pentene and 86% *E*-2-pentene. This ratio is different from that obtained from *E*-1,3-pentadiene hydrogenation (~5% conversion, 23% 1-pentene, 5% *Z*-2-pentene and 71% *E*-2-pentene) in absence of the *Z*-isomer, suggesting that in our system *Z*-1,3-pentadiene is not isomerised to *E*-1,3-pentadiene before hydrogenation. Our results are more in agreement with those of Wells and Wilson [9] who examined the hydrogenation of the *Z*- and *E*-1,3-pentadiene separately in the gas phase and found only limited isomerisation from *Z* to *E* and no isomerisation from *E* to *Z*. No isomerisation was observed in our system when *E*-1,3-pentadiene was hydrogenated. Also they [9] observed all three pentene isomers from each pentadiene isomer.

The *Z*/*E*-1,3-pentadiene mixture also has a different effect on catalyst deactivation compared to the *E*-isomer. Less material is deposited on the catalyst; by the end of the run the ratio of C-5 molecules retained by the catalyst to Pd atoms in the system is approximately 30:1 compared with 100:1 for the *E*-isomer in the absence of the *Z*. This effect could be related to an inhibition of surface polymerisation due to a change in the adsorbed conformation. If this were to be the case then we may look to see what other effect this has on the reaction. The reduction in the rate of hydrogenation of *E*-1,3-pentadiene may also reflect this change in conformation. If the addition of the *Z*-1,3-pentadiene were to break up a π-stacking formation of *E*-1,3-pentadiene on the surface, it may well reduce both the activity and the facility for polymerisation.

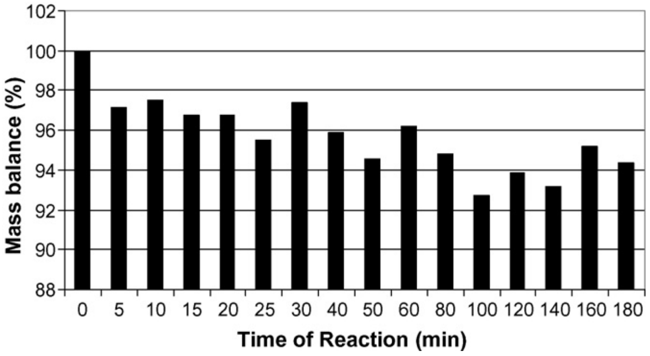
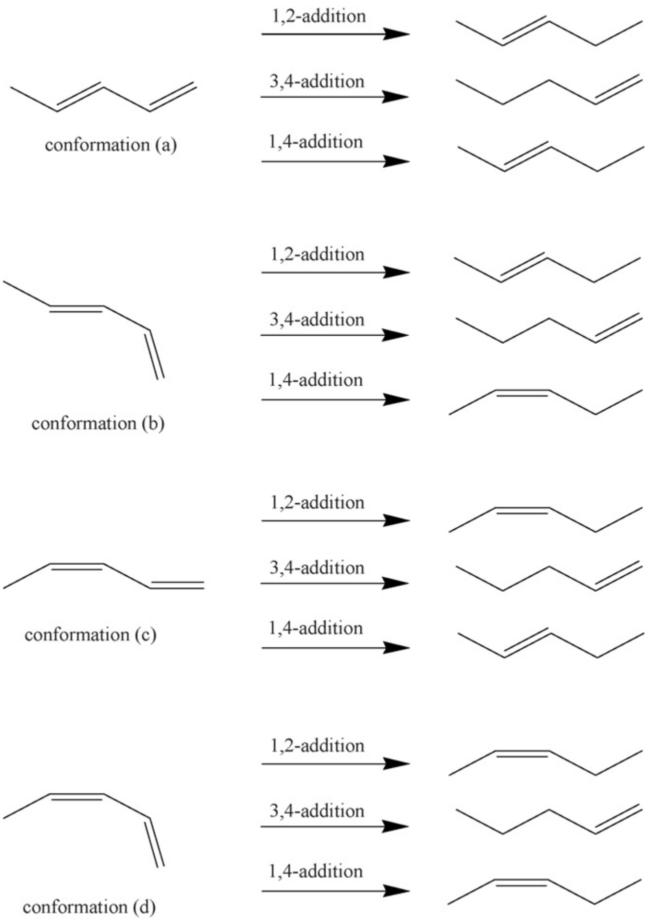


Fig. 4. Mass balance during hydrogenation of *E*-1,3-pentadiene.



Scheme 2.

When the selectivity is compared at 50% conversion (Table 1) it can be seen that the system with the lowest alkene selectivity is the *Z*/*E* mix with an alkane selectivity of 44%. While *E*-1,3-pentadiene gave the lowest alkane yield. The alkane yield reflects the extent of deactivation in the system, with the *E*-isomer having the greatest deactivation. The alkene isomers are all considerably removed from the thermodynamic mix of 81, 17.5, and 1.5% for *E*-2, *Z*-2 and 1-pentene, respectively, indicating that isomerisation is slow after the initial stages, i.e. isomerisation is also affected by the deactivation. However, it is interesting to note that the *Z*/*E* ratio for the mono-ene is at equilibrium for the *Z*/*E*-1,3-pentadiene hydrogenation, suggesting that *Z*/*E* isomerisation may be more facile than terminal/internal bond shift.

When there is competitive hydrogenation between 1,4-pentadiene and 2-pentyne, the rate constant for 1,4-pentadiene increases as does the rate constant for 2-pentyne. This behaviour is similar to that found when a 1-pentene/2-pentyne mix was hydrogenated [8] although in that case only the 1-pentene rate increased while the 2-pentyne was relatively unchanged. Examining the effect on the pentene isomer formation (Table 3) reveals that the isomer pattern is not a simple additive function of each component at the appropriate conversion. The initial isomer mix for 2-pentyne has no 1-pentene and very high *Z*-2-pentene, while the equivalent point for 1,4-pentadiene has very high 1-pentene and very low *Z*-2-pentene. However, the mixed reaction gives an initial isomer distribution of 14% 1-pentene, 57% *Z*-2-pentene and 29% *E*-2-pentene. Clearly the hydrogenation of 2-pentyne is favoured as witnessed by the high *Z*-2-pentene selectivity but it is the level of *E*-2-pentene that is unusual. Neither reactant has a high selectivity to *E*-2-pentene in the initial stages, yet it is now more favoured than 1-pentene. As time and conversion move on the respective ratios change and by the conversions reached in Table 3, *E*-2-pentene is the least favoured isomer. These results show that the two hydrogenations do affect the isomerisation reaction even though both produce isomer ratios that are well removed from equilibrium. In a previous study [8] it was proposed that ‘‘increasing the concentration of subsurface hydrogen and/or more effective transfer of sub-surface hydrogen to the reactant could achieve rate enhancement’’. In the present study the influence on isomer ratio as well as the rate may suggest that subsurface hydrogen plays a role in both processes. Sensitivity to hydrogen pressure for 1,3-butadiene hydrogenation and butane isomerisation was also suggested by Rupprechter and co-workers [12] to explain the effect of carbon monoxide on the hydrogenation of 1,3-butadiene over Pd (1 1 0).

When 1,3-pentadiene and either 1- or 2-pentyne are hydrogenated in competition, the rate of reaction is reduced for both reactants. This is indicative of competitive adsorption and a reduction in the hydrogen availability. This would indicate that there were at least two sites on the catalyst, one for the conjugated diene, one for the alkyne and potentially one for hydrogen. This is in keeping with a recent study of 1-pentyne hydrogenation where a specific site was created by the alkyne in contrast to the alkene [13]. This would also agree with an adsorption study involving 1,3-butadiene, propyne and CO [14], which indicated that propyne and CO accessed the same site but the conjugated diene accessed another site. When the single reactant is present hydrogen can access the sites that are inaccessible for the organic however when both diene and alkyne are adsorbed the concentration of hydrogen is significantly reduced. This is further supported by the alkene selectivity, which is increased in the competitive system relative to the single reactant at equivalent conversion. It is equally in keeping with the study by Rupprechter and co-workers [12] except in our case the alkyne takes the role of the carbon monoxide in inhibiting hydrogen concentration. The isomer ratios can be modelled quite closely assuming independent reactions (Table 3).

5. Conclusions

In this study we have shown the difference in reactivity between conjugated and non-conjugated systems both when reacted on their own and when reacted in competition with alkynes. The non-conjugate molecule, 1,4-pentadiene, reacts in a manner similar to 1-pentene, whereas the conjugated 1,3-pentadiene is more complex. Reaction with and alkyne results in a highly interactive system when 1,4-pentadiene is the reactant, while with 1,3-pentadiene the alkyne and alkadiene appear to react separately.

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