1 Introduction

The petrochemical industry has relied on the oligomerisation of short-chain olefins for blending into fuels since 1935 (Ipatieff *et al.*, 1935). Oligomerisation of short-chain olefins allows a refinery a means to incorporate lighter boiling olefins into the fuel pool and still comply with volatility specification. These short-chain olefins originate from fluid catalytic cracking (Cruz *et al.*, 2007; Chen *et al.*, 2008), steam-cracking and dehydrogenation units (Di Girolamo *et al.*, 1997). In high-temperature Fischer-Tropsch processes, short-chain alpha olefins (C_3-C_4) are also continually produced and then oligomerised (Dancuart *et al.,* 2004). Olefins present in the light naphtha fraction (specifically C_5-C_6 carbon number) are not oligomerised and instead used as feedstock for other chemical production processes (De Klerk, 2005b; Dancuart *et al.*, 2004). However, with the continued increase in global demand for fuel and international concern about dwindling oil resources (Bentley, 2002), it is increasingly becoming economically feasible to incorporate a wider range of product into the fuel pool.

The quantity of light boiling olefins that can be blended into fuel is restricted by volatility limitations, as stated earlier. These limitations will become even more significant when environmental concerns may result in the future mandatory addition of ethanol to fuels (Schmidt *et al.*, 2008). Oligomerisation/dimerisation of the C_5-C_6 olefins will result in greater flexibility for the petrochemical industry in terms of the olefin fraction that can be blended into the fuel. Oligomerisation of longer chain olefins can also be used for the production of lubrication oils (Dazeley, 1948; Sarin *et al.*, 1996) or detergents and plasticisers (Da Rosa *et al.,* 1997). Making it increasingly more important to study the oligomerisation/dimerisation reactions for these longer-chain olefins. 1-Hexene forms a substantial part of the naphtha fraction from Fischer-Tropsch processing (De Klerk, 2006a) and was selected as a model component to study these oligomerisation reactions.

Various catalysts have been investigated for the oligomerisation of olefins, examples of which include liquid phosphoric acid (Ipatieff, 1935), solid phosphoric acid (Ipatieff and Corson, 1935), sulphuric acid (Naworski and Harriott, 1969), Aluminum Chloride (Dazeley, 1948), Cobalt-Oxide-on-Carbon (Schultz, 1967), ZSM-5 (Tabak *et al.*, 1986), Ni-Aluminosilicates (Bercik *et al.*, 1978), cation exchange resins (O'Connor *et al.*, 1985) and silica-alumina (Shepard *et al.,* 1962). These are just some of the catalyst that is active for oligomerisation, a more comprehensive list can be found in the reviews of Schemrling and

Ipatieff (1950) and Skupińska (1991). Commercially oligomerisation has occurred using ZSM-5 (Tabak *et al.,* 1986), solid phosphoric acid (SPA, De Klerk, 2007a) and Ni (Commereuc *et al.,* 1982). Due to the ban of MTBE from fuel MTBE, cation exchange resins have also been investigated for the dimerisation of iso-butene (Hondela and Krause, 2003). SPA, which is used in this investigation, is manufactured by mixing diatomaceous earth (Kieselguhr) with liquid phosphoric acid (Coetzee *et al.*, 2006). The resultant catalyst consists of a layer of different phosphoric acid species, i.e. ortho, pyro, tri and poly phosphoric acid (the free acid layer), supported on a mixture of silica and silicon phosphates and is therefore known as a liquid supported catalyst. Although the silicon phosphates affect the crushing strength of the catalyst, it is accepted that the phosphates have no influence on the catalytic activity of SPA (Krawietz *et al.,* 1998).

Most of the previous work on oligomerisation reaction rates focused on the oligomerisation of shorter-chain olefins such as propene and butene (Cruz *et al.*, 2007; Honkela and Krause, 2004; Alcántara *et al.*, 2000; Cao *et al.*, 1988). There are relatively few investigations into the oligomerisation of longer-chain olefins. Where these reactions were studied, the focus was on the behaviour of various isomers at fixed residence times, without giving any consideration to the progression of the reaction. For example, during the alkylation reaction of hexene, Nel and De Klerk (2007) found that linear hexenes were selectively alkylated and branched hexenes selectively dimerised. This selective oligomerisation of branched olefins over SPA, was corroborated by De Klerk (2006b) for octene dimerisation. This indicates that skeletal isomers present in the feed is critical to the oligomerisation of heavy olefins over SPA.

Studies specifically on the oligomerisation of C_6 olefins investigated the catalyst activity at a constant residence time instead of investigating the reaction progression (Van Grieken *et al.*, 2006; Pater *et al.*, 1999). For the oligomerisation of butenes, Golombok and de Bruijn (2000) show that there is a difference in the fuel quality, depending on which double bond isomer is present initially. This observation could however be limited to oligomerisation of olefins over Amorphous Silica Alumina since the catalyst contains both Lewis and Brønsted acids since Golombok and de Bruijn (2000). For the oligomerisation of longer-chain olefins, such as 1-hexene, an even greater quantity of isomers – including skeletal isomers (Quan *et al.*, 1988) – can form part of the isomer community that contributes to the oligomerisation reaction. The reaction progression of the various isomerisation and subsequent oligomerisation reactions will then be important, since the reaction progression can influence the product selectivity. Not only is the product reaction route important but also the

temperature dependence of these rates. Due to differences in the activation energy, for each reaction rate, changing the reaction temperature could influence the product distribution. Therefore it is increasingly important not only to study the oligomerisation capabilities of the catalyst at fixed residence times, but also to gain an insight into the temperature-dependent reaction progression of the various isomers. Accordingly, in Chapter 3 the batch reaction kinetics of the dimerisation of 1-hexene is discussed regarding the temperatures around which the current oligomerisation reactors for shorter chain olefins are operated. The quality of the produced fuel will not only depend on the amount of dimerised product, however, but also on the degree of cracking and secondary oligomerisation that takes place after dimerisation. Hence, the effect of temperature and residence on the degree of cracking is also discussed in Chapter 3.

When studying the oligomerisation of propene on SPA, Cavani *et al.* (1993) report that a low water feed content is preferable where the reaction rate is concerned. The water in the reaction mixture is absorbed into the free acid layer of the catalyst and directly influences the acidity and activity of the catalyst. In addition, a variation in water content is also reported to have an influence on reaction selectivity. For instance, Prinsloo (2006) showed that there was increased diesel selectivity with decreased hydration levels for the oligomerisation of propene over SPA. De Klerk *et al.* (2006) also found that the hydration of the SPA as well as the reaction temperature affected the quality of the produced fuel when butene was oligomerised.

Phosphoric acid reacts with water to form an equilibrium distribution of the various acid oligomers, $H_{2n}P_nO_{3n+1}$: from the less condensed ortho phosphoric acid, to the more condensed pyro and tri phosphoric acids and finally to the highly condensed poly phosphoric acids (Jameson, 1959). Altering the water content on the catalyst will therefore affect the resulting acid strength as well as the composition of the phosphoric acid. Although Zhirong *et al.* (2000) report no definite trend in the total quantity of free phosphoric acid and the catalytic activity of SPA towards propene oligomerisation, they did find that the presence of pyro phosphoric acid in the free acid layer is imperative for the catalytic activity.

In Chapter 4 attention is given to the influence of acid strength and free acid content on the reaction kinetics and the product distribution. Batch kinetic data was gathered for various acid strengths by either *1)* altering the hydration of the catalyst at different temperatures or *2)* investigating the effect of altering the free acid content of the catalyst at a constant temperature of 200 °C. The vapour liquid equilibrium data of phosphoric acid together with the measurements of the free acid content after various catalyst treatment procedures, was

used to alter the P_2O_5-based acid strength and subsequently the distribution of acid oligomers in the free acid layer.

The product from the oligomerisation of 1-hexene over SPA could either be used as lubricating oil, for detergent production, or as fuel additive. The use of the product, as either, is limited by the chain length and the degree of branching of the product. Since acid strength can be assumed to affect the degree branching and chain length of the formed product, this will impact the use of the 1-hexene oligomerate over SPA. In Chapter 5 the effect of acid strength on the degree of branching and chain length of the product is discussed.

2 Literature survey

Oligomerisation of short chain olefins is by no means a new technology as it has been practised industrially since 1935 (Egloff, 1936; Ipatieff *et al.,* 1935). Reaction kinetics for oligomerisation over SPA has mostly been overlooked owing to the extent of the experimental data needed to gain an accurate kinetic model. For this reason the literature has focused on gaining insights into the effect of operating conditions and feed concentration on the quality of the produced fuel (Ipatieff and Schaad, 1938).

A literature survey is needed to understand the oligomerisation of short chain olefins over SPA so as to convey aspects of the quality of the fuel, the reaction network/mechanism, reactivity and selectivity differences of isomers, the catalyst (with regard to composition, hydration and acid strength) and the attempts that have been made to model the reaction kinetics in the literature.

2.1   Oligomerisation: Product slate

Oligomerisation of olefins can be used for the production of various products from lubrication oils, detergents and plasticiser feed stock to the production of fuels (gasoline, jet fuel and diesel). Since a large part of the literature focuses on the production of fuels from short chain olefins a basic understanding of the product slate and the properties of the product is needed.

For the production of fuels, short chain olefins are oligomerised and then fractionated into petrol, jet fuel and diesel with the cut-off points dictated by the applicability of the product to each fuel. If paraffinic hydrocarbons are considered, chain length 1 to 4 can be regarded as liquefied petroleum gas (LPG), 5-9 can be incorporated into petrol/gasoline, 11-22 can be used as diesel or jet fuel depending on the degree of branching (Dancaurt *et al.,* 2004).

To define the quality of petrol engine testing is used determine the tendency of the gasoline to auto ignite under compression, which results in knocking. For octane testing a baseline is used whereby the octane rating of 1-heptane equals zero with iso-octane (trimethyl pentane) equalling 100. For streams consisting of paraffins and olefins, the octane rating is influenced by the following:

- The chain length of the hydrocarbon: with an increase in the chain length, the octane is generally expected to decrease (if both molecules have the same branching).

- The degree of branching: with an increased degree of branching, at a fixed carbon length, the octane value is expected to increase. This is important to the oligomerisation of short chain olefins, since isomerisation and oligomerisation of short chain olefins can both occur over acid catalyst. The relative ratio of each will affect the quality of the petrol.

- The saturation of the hydrocarbon (a saturated hydrocarbon has no double/triple bonds, e.g. alkanes): unsaturated hydrocarbons tend to have a greater octane value than saturated hydrocarbons. The fraction of unsaturated hydrocarbons that can be blended into the fuel is however regulated, the Euro 4 specification for olefin content is 18% (De Klerk *et al.*, 2004)

The specifications of jet fuel and diesel overlap with regard to flash point and final boiling point, the big difference between diesel and jet fuel lies in the CFPP, freezing point and cetane. For jet fuel a low freezing point is needed (maximum freezing point of -47 °C, US Ministry of Defence Standard 91-91 Issue 6), where as for diesel a CFPP (which is a function of freezing point) between 0 and -20 °C is defined depending on the season (DIN EN 590-2009 standard). The freezing point, and CFPP, of a hydrocarbon is dependent the degree of branching, increasing the degree of branching reduces both the freezing point and CFPP. The cetane value, however, is larger for a linear hydrocarbon. Therefore if the product boils above the petrol fraction, the fuel would be more applicable as a jet fuel if the product is highly branched or as diesel if the product is highly linear.

Lubricating oils are paraffinic hydrocarbons with a chain length greater than 20 and shorter than 40 which are prevalently branched (Montanari *et al.*, 1998). Whereas for the synthesis of detergents and plasticisers, shorter chain linear ($<C_{20}$) olefins are required (Da Rosa *et al.,* 1996).

2.2   Background: Oligomerisation of short chain olefins over SPA

Industrially, mainly two catalysts are used for the oligomerisation of short chain olefins to gasoline, namely solid phosphoric acid (Ipatieff *et al.*, 1935) and ZSM-5 (Tabak *et al.*, 1986) which are used by UOP and Mobil respectively. Oligomerisation of short chain olefins have also been shown to occur thermally (Ipatieff and Pines, 1936), although the addition of a catalyst reduces the severity needed for oligomerisation.

Historically SPA was used for the upgrading of light olefins, both propylene and butenes, to fuel (Ipatieff *et al.*, 1935;Weinert and Egloff 1948; Deeter, 1950; Egloff and Welnert, 1951).

The feed to a Catalytic Polymerisation unit can originate from Fischer-Tropsch, catalytic cracking or thermal cracking, typical analysis of which is shown in Table 2-1 (Jones, 1956; De Klerk *et al.*, 2006). As is evident from the feed composition, a wide variety of olefins are fed into the reactor. This creates an assortment of dimerisation and co-dimerisation reactions which may occur; if the reaction rate between these isomers differs, a large reaction network would be required especially if the RON values differ among the varied products.

Table 2-1: Composition of feed to a catalytic polymerisation unit from Fischer-Tropsch, thermal cracking and catalytic cracking.

Component	C4 FT cut	Thermal cracking	Catalytic cracker
Hydrogen		2.1%	
Methane		31.1%	
Ethylene		19.1%	
Ethane		31.2%	0.1%
Propene		8.3%	14.4%
Propane	<0.1%	2.2%	15.9%
2-methyl-propane	4.5%		
n-butane	22.1%	4.1%	14.5%
iso-butane			22.0%
trans-2-butene	2.0%		
1-butene	54.8%	1.1%	32.8%
Butadiene		0.0%	0.1%
2-methyl-propene	5.7%		
Cis-2-butene	3.4%		
2-methyl-butane	0.4%		
n-pentane	0.2%	0.7%	0.1%
3-methyl-1-butene	1.7%		
2-methyl-2-butene	3.7%		
2-methyl-1-butene	0.2%		
other C5+ material	1.3%		

The quality of the produced gasoline is also dependent on the feed composition, if propylene is fed to the reactor the hydrogenated RON of the fuel would be less than 80, whereas if butenes are fed to the reactor a hydrogenated RON between 90-96 is viable (Egloff and Welnert, 1951). This is due to isomerisation which occurs readily over SPA. During the oligomerisation of 1-butene over SPA at mild operating conditions (< 250°C), the C_8 product spectrum indicated that isomerisation had indeed occurred before the butene oligomerised (De Klerk, 2004). Since the isomerisation of the product will improve the

quality of the gasoline, the induction of isomerisation is critical to the production of a high RON fuel (De Klerk 2004; Nel and De Klerk, 2007; Cowley *et al.*, 2006).

Unlike propylene butene has a skeletal isomer, iso-butene, which is known to influence the reaction rate and the degree of branching of the produced fuel (i.e. RON). This has bearing on the oligomerisation of 1-hexene since hexene has various branched isomers which could react differently to their linear counter parts. Ipatieff and Schaad (1938) showed that with a more pronounced presence of isobutene, not only did the oligomerisation occur more easily at less severe operating conditions but the quality of the produced fuel also improved (Table 2-2). Controlling the degree of branching in the feed is therefore important for increasing the reaction rate and optimising the quality of the gasoline produced.

Table 2-2: Effect of isobutene on oligomerisation rate and the quality of the hydrogenated produced fuel.

T (°C)	Butenes charged ($g_{butenes}$/(hr.cc$_{cat}$))	Isobutene percentage	Total conversion	Octane no.
80	4.75	84.8%	91.5%	98
95	6.95	96.0%	88.0%	100
120	5.40	91.4%	87.0%	98
120	1.37	46.0%	74.0%	97
120	0.58	36.5%	54.0%	96
120	0.32	25.5%	49.0%	95
149	0.87	27.1%	58.0%	95
177	0.88	0.0%	72.0%	83
177	0.77	1.4%	64.0%	85

The position of the double bond also affects the reaction rate. Paynter and Schuette (1971) noted selectivity differences for a constant feed olefin content of C_3 and C_4 olefins, depending on the fraction of 1-butene and 2-butene in the feed. As more 2-butene was introduced in the feed, the selectivity turned toward the dimerisation of C_3 and less C_4 dimerisation and co-dimerisation took place. Cao *et al.* (1988) determined that 2-butene was far less reactive than 1-butene for the oligomerisation of a light olefin feed over SPA at 115 °C. It should be noted that at temperatures below 550 °C the equilibrium distribution of butenes favours 2-butene above 1-butene. Hence to obtain a correct measurement of the

reaction rate difference between the two isomers, the equilibrium distribution should be taken into account as well as measuring the rate difference for the two isomers experimentally. Cao *et al.* (1988) took the equilibrium distribution into account but did not have kinetic data available for the two individual isomers. This could result that the difference in reaction rate predicted could be lumped in an inadequate reaction mechanism and not due to difference in the reaction rate for the two isomers. De Klerk (2004) however showed that for the oligomerisation of a pure mixture of 1-butene, cis-2-butene and trans-2-butene showed that 1-butene had a far higher conversion at the same temperature and residence time in a pack bed reactor. The presence of 1-butene seemed to ease the formation of iso-butene which reacts to far more significantly than its linear counterparts. The increased probability of 1-butene to isomerise was also present in the formation of highly branched product from 1-butene.

Golombok *et al.* (2000) found that the quality of the produced fuel would also differ; depending on which of these two olefins oligomerised, a superior gasoline was obtained for the oligomerisation of 1-butene in comparison to the 2-butene oligomerisation. The work was however done on Amorphous Silica Alumina which is both a Lewis and Brønsted acid for which the reaction pathway may differ from SPA which is predominantly a Brønsted acid. For butene oligomerisation over SPA De Klerk (2004) observed that the formation of trimethyl pentene was linked to the concentration of 1-butene and iso-butene in the reaction mixture, there for in an equilibrated mixture of n-butenes the oligomerisation to trimethyl pentene occurs through the 1-butene in the mixture. This further creates the impression that the distribution of isomers in the reaction mixture controls the fuel quality.

Since kinetic data is not available for complex mixtures of olefins, experimental studies rely on the comparison of the fuel quality at various space velocities to draw residence time-dependent trends to the quality of the fuel. For a mixed butene feed at 150 °C and 38 bars, De Klerk *et al.* (2004), showed that at high space velocities conversion dropped whereas the RON of the fuel increased (Figure 2-1). Since the selectivity to branched C_8s influences the resulting octane, it becomes a problem to limit the selectivity to the dimerised product, especially at lower space velocities which are needed to obtain high conversion.
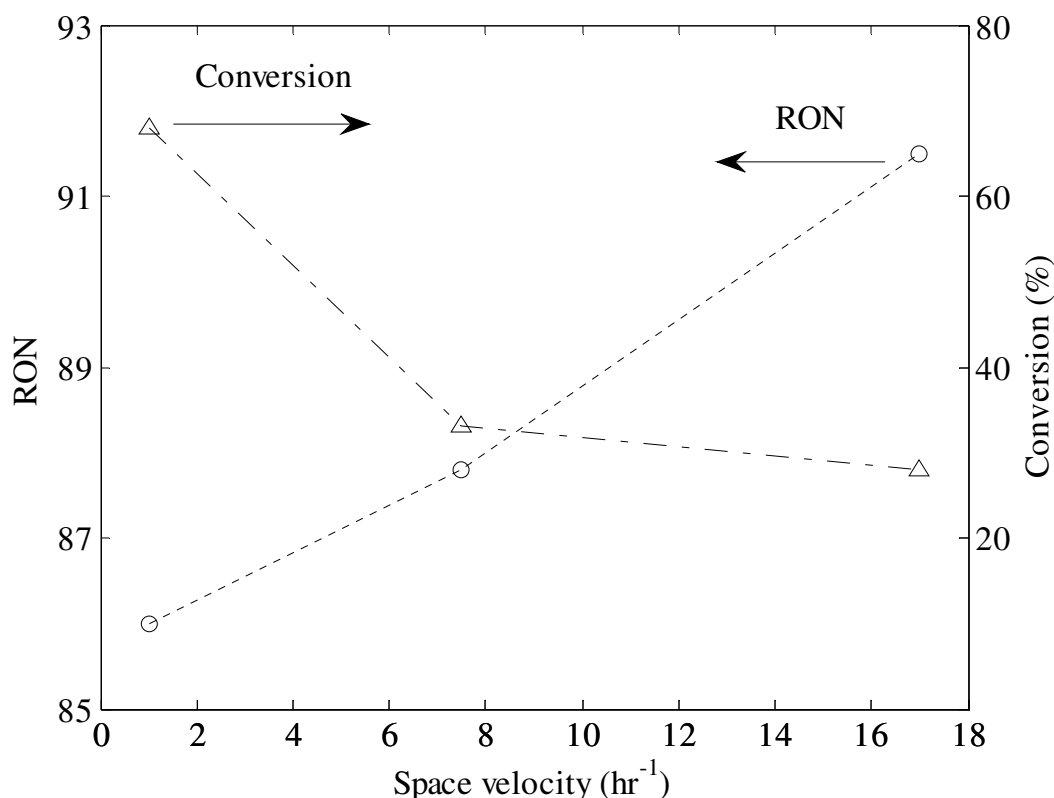
Figure 2-1: Effect of space velocity on the conversion and RON for the oligomerisation of C4 olefins over SPA, |● – RON, ▲ - Conversion (De Klerk, *et al.*, 2004).

A kinetic model would be invaluable if the increase in RON could be incorporated over the progression of the reaction. For the kinetic model to predict the rate of oligomerisation, and possibly estimate the RON, the model would have to incorporate the difference in the reactivities of olefins, together with the rate of isomerisation. This could easily result in a substantial number of parameters that would be required to model the reaction network.

2.3   Oligomerisation of light naphtha olefins over SPA

Industrial oligomerisation mainly focuses on the refining of shorter chain olefins ($<C_5$) into the fuel pool. Naphtha range products can easily be blended into the gasoline pool without further refining but the extent that can be blended is limited by the linearity of the naphtha. The oligomerisation (or isomerisation) of the naphtha fraction will allow the incorporation of a larger fraction into gasoline, jet fuel or diesel (Quan *et al.*, 1988; De Klerk, 2005b).

Early work on the dimerisation of a pentene mixture over SPA by Ipatieff and Schaad (1948) showed that pentene skeletal isomers can be dimerised over SPA at low temperatures

(83 and 100 °C). The rate was found to be faster for the dimerisation of 2-methyl-1-butene than that of 3-methyl-1-butene at similar reaction conditions. Unfortunately no comparison was available for the dimerisation of 1-pentene which would give valuable information to the route of dimerisation of longer chain olefins (e.g. via skeletal isomerisation or direct dimerisation of linear pentene isomers). As such fairly little could be extracted for the path of heavy olefin oligomerisation over SPA.

Where heavier olefins have been oligomerised over SPA, the high degree of branching seen in the product indicates the catalyst is more appropriate for the production of gasoline or jet fuels. Mashapa *et al.* (2007) focused on the effect of oxygenates on the oligomerisation of heavy olefins, however experiments done for a 1:1 mass ratio in the feed of butenes and hexenes showed that 76% and 91% of the 1-hexene converted at 150 and 180 °C respectively. Although this was higher than the extent of butene conversion, which was 27% and 44%, only 18% and 30% of the hexenes converted to oligomers (1-hexene predominantly converted to hexene isomers). Interestingly the carbon distribution of the product was also limited to the formation of dimerised product. This limited extent of oligomerisation over SPA was also noted for the alkylation of benzene with 1-hexene by Nel and De Klerk (2007). This low extent of oligomerisation with high branching negates the use of SPA for the production of lubricating oils as well as detergents and plasticisers. Therefore it seems that SPA is purpose built for the production fuel range products.

A study done by De Klerk (2006b) investigating how the degree of branching of a C_8 olefin influences the rate of dimerisation indicates that trimethyl pentene is more reactive than 1-octene at similar operating conditions. This suggests that for the oligomerisation of longer chain olefins, isomerisation needs to occur first before oligomerisation can occur. This limits the use of SPA as a catalyst for the oligomerisation of long chain alpha olefins. Due to a reduction in activity with chian length, the temperature needs to be upped until isomerisation becomes viable. Unfortunately if the temperature is raised too much coke formation will inevitably occur more freely limiting the usefulness of the catalyst. Therefore when oligomerising of light naphtha olefins to diesel, the reaction is usually catalysed by a Zeolite (Pater *et al.*, 1998; Pater *et al.*, 1999; Garwood, 1983), silica alumina (Van Grieken *et al.*, 2006; Escola *et al.*, 2006) or Ni (Fortini *et al.*, 1997; Heveling *et al.*, 2003).

When SPA is used as catalyst for the oligomerisation of longer chain olefins, the reaction rate seems to be limited by the rate of isomerisation, however no kinetic data is available for predicting the route or relative rate of dimerisation through skeletal or linear olefin isomers. If the reaction conditions could be varied to overcome this limitation, SPA would be more

viable. It also seems that due to the high degree of branching incurred by the isomerisation over SPA, SPA is more applicable for the production of a jet fuel than a diesel fuel or lubricating oils.
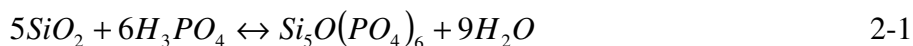
2.4 Solid phosphoric acid

The patent by UOP for the production of SPA has existed since 1962 (Morrell, 1962a; Morrell, 1962b; Morrell, 1964). The support on which the phosphoric acid is placed has mainly been diatomaceous earth (kiezelguhr) although the phosphoric acid has also been impregnated on quartz (Langlois & Walkey, 1951; Langlois & Walkey, 1952; Vinnik and Obraztsov, 1983) and silica gel (Kotsarenko *et al.*, 1989). Mainly kiezelguhr, such as Celite (Handlos and Nixon, 1956), is preferred as support for impregnating phosphoric acid.

When discussing SPA, certain key concepts create confusion if there is no prior knowledge of the catalyst. The catalyst is described in terms of the acid impregnated on the catalyst:

- *firstly* the total acid content describes the total quantity of acid present on the catalyst (as a weight percentage of the catalyst),
- *secondly* the "*free acid*" is used to describe the quantity of phosphoric acid present as a liquid layer in the catalyst (this excludes the quantity of chemically bound phosphoric acid on the support) and this is expressed as the weight percentage H_3PO_4 with regard to the catalyst weight,
- *thirdly* the acid strength, this describes the phosphoric acid strength of the free acid (this concept will be further elaborated in this section).

SPA is produced by mixing kiezelguhr and phosphoric acid at 200 °C (impregnation temperature) before being extruded. After extrusion, the catalyst is calcined for a predetermined length of time. During the impregnation of the kiezelguhr, the phosphoric acid bond to the silicon support and silicon phosphates originate:

Silicon ortho phosphate:

$$5SiO_2 + 6H_3PO_4 \leftrightarrow Si_5O(PO_4)_6 + 9H_2O \qquad \text{2-1}$$

Silicon pyro phosphate

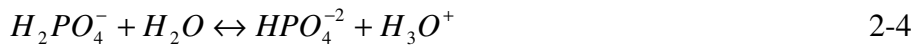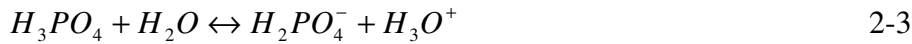$$5SiO_2 + 10H_3PO_4 \leftrightarrow 5SiP_2O_7 + 15H_2O \qquad \text{2-2}$$

The total phosphoric acid content in the catalyst is present as either fixed phosphorus (silicon phosphates; Equation 2-1 and 2-2) or as free acid. The total acid content of SPA is in

the order of 70%. Most of the phosphorous present in the catalyst is fixed on the support as silicon phosphates, whereas only about 20% of the acid is present as free acid (Coetzee *et al.*, 2006). The free acid on the catalyst is critical to the activity of SPA since the support (fixed phosphorous) does not contribute to the activity of the catalyst. Therefore only the supported free acid determines the activity of the catalyst (Krawietz *et al.*, 1998). The reactivity of silicon phosphates to oligomerisation is however not so simple to measure, since a small amount of water present in the feed will result in the hydration of the silicon phosphates to phosphoric acid, resulting that no forthright conclusion can be made concerning the activity or non-activity of the silicon phosphates (Schmerling and Ipatieff, 1950).
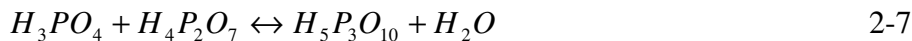
A study by Prinsloo (2007) on the production of SPA from low-quality kieselguhr showed that quartz had a negative affect on the crushing strength of the catalyst. It is believed that the crushing strength is of critical importance to the industrial applicability of the catalyst. The pressure drop measured during the operation of the catalyst has shown a steady increase with time on stream; this is coupled to the disintegration of the catalyst which is directly related to the crushing strength of the catalyst (Coetzee *et al.*, 2006). The two most important aspects of the catalyst, industrially, are its crushing strength and activity. Both of these properties are influenced by the acid strength of the phosphoric acid used for impregnation, the calcination temperature and the type of kiezelguhr impregnated. An increase in both the acid strength and the calcination temperature is beneficial to the crushing strength. This is connected to the formation of the silicon pyro phosphates, which is directly linked to the physical properties of the catalyst. However, when increasing these parameters, the free acid content of the catalyst decreases, meaning the activity decreases (Coetzee *et al.*, 2006).

As stated above, the free acid layer of phosphoric acid determines the activity of the catalyst. Therefore in order to investigate the catalyst, the properties of the free acid layer should be understood. Since the free acid layer is entirely composed of phosphoric acid, the properties of phosphoric acid have to be investigated.

Phosphoric acid (H_3PO_4) is a triprotic acid, meaning that the dissociation of phosphoric acid occurs three times (Equation 2-3 to 2-5). For each successive disassociation, the equilibrium shifts less to the formation of H_3O^+ ($Ka_1 = 7.5 \times 10^{-3}$, $Ka_2 = 6.2 \times 10^{-8}$ and $Ka_3 = 2.14 \times 10^{-13}$). As the first dissociation constant is significantly larger than the last two, the acid strength is determined by the first dissociation constant (Kotz & Treichel, 1999).

$$H_3PO_4 + H_2O \leftrightarrow H_2PO_4^- + H_3O^+ \qquad\qquad 2\text{-}3$$

$$H_2PO_4^- + H_2O \leftrightarrow HPO_4^{-2} + H_3O^+ \qquad\qquad 2\text{-}4$$

$$HPO_4^{-2} + H_2O \leftrightarrow PO_4^{-3} + H_3O^+ \qquad\qquad 2\text{-}5$$

Generally the activity of a catalyst is stated in terms of the equivalents of H^+. For this reason, the degree of dissociation is a measure of the activity. This is not so simple for phosphoric acid, because phosphoric acid condenses to form stronger acids, e.g. ortho phosphoric acid (H_3PO_4) $\rightarrow$ pyro phosphoric acid ($H_4P_2O_7$, Equation 2-6) $\rightarrow$ tri phosphoric acid ($H_5P_3O_{10}$, Equation 2-7), etc. For pyro phosphoric acid, ($H_4P_2O_7$) the first and second dissociation constants are 1.4×10^{-1} and 3.2×10^{-2} respectively, which are much larger than that of ortho phosphoric acid. This indicates that the more condensed the acid, the stronger the resulting acid (Weast, 1988).

$$2H_3PO_4 \leftrightarrow H_4P_2O_7 + H_2O \qquad\qquad 2\text{-}6$$

$$H_3PO_4 + H_4P_2O_7 \leftrightarrow H_5P_3O_{10} + H_2O \qquad\qquad 2\text{-}7$$

Since phosphoric acid can condense, it is not easy to describe the condensed state of the phosphoric acid present in the free acid layer without analysing the free acid. The chemical composition of the phosphoric acid depends directly, on the quantity of water present in the free acid. Various methods are used to express the acid strength of the catalyst. One method of describing the acid strength is the fraction phosphorous oxide (P_2O_5). This started because of the production of various strengths of phosphoric acid by mixing P_2O_5 with water (Equation 2-3). Another method of expressing the acid strength is by means of the weight percentage H_3PO_4. Starting with pure ortho phosphoric acid, different acid strengths can be obtained by evaporating water from the mixture. Converting between the two methods is done by the stoichiometry of mixing P_2O_5 with water to form H_3PO_4 (Equation 2-8). The conversion factors used to convert between the two methods are shown in Table 2-3.

$$P_2O_5 + 3H_2O \leftrightarrow 2H_3PO_4 \qquad\qquad 2\text{-}8$$

Table 2-3: Unit conversion between % P_2O_5 and % H_3PO_4

Compound	Chemical Formula	Molar weight [kg/kmol]	P_2O_5 [wt. %]	H_3PO_4 [wt. %]
Phosphorous pentoxide	P_2O_5	142	100	138
Ortho phosphoric acid	H_3PO_4	98	72.4	100

This still does not describe the condensed form (i.e. ortho/pyro) in which phosphoric acid will be present, it only describes the fraction of P_2O_5 and water in the acid. Jameson (1959) established how the condensed state of phosphoric acid changes by mixing P_2O_5 with water, the dependence of the acid distribution with the fraction of P_2O_5 in the mixture is shown in Figure 2-2. Below 68% P_2O_5 the acid mixture shifts completely to ortho phosphoric acid, changing to more condensed acids as the water fraction in the phosphoric acid decreases.

For the evaporation of a mixture of phosphoric acid and water, a vapour-liquid equilibrium will ensue, altering the water (or phosphoric acid content) of the liquid which will then influence the acid strength of the phosphoric acid. Brown & Whitt (1952) determined the phase equilibria for various mixtures of P_2O_5 and water (Figure 2-3). At temperatures below 300 °C phosphoric acid's vapour pressure becomes negligible and the vapour phase will contain mostly water. Increasing the temperature above 300 °C will therefore result in the evaporation of phosphorous from the catalyst.
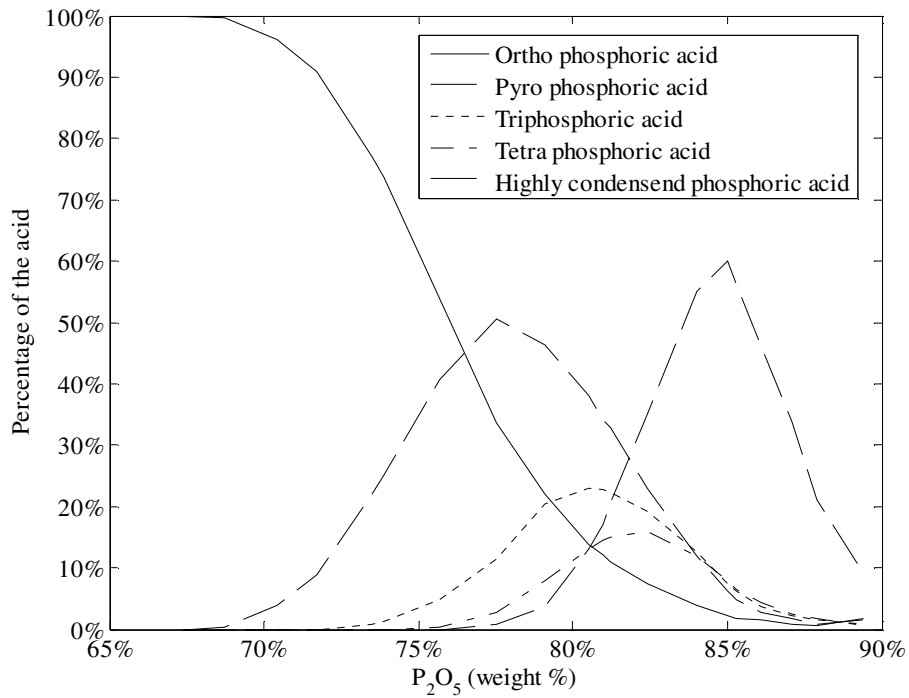
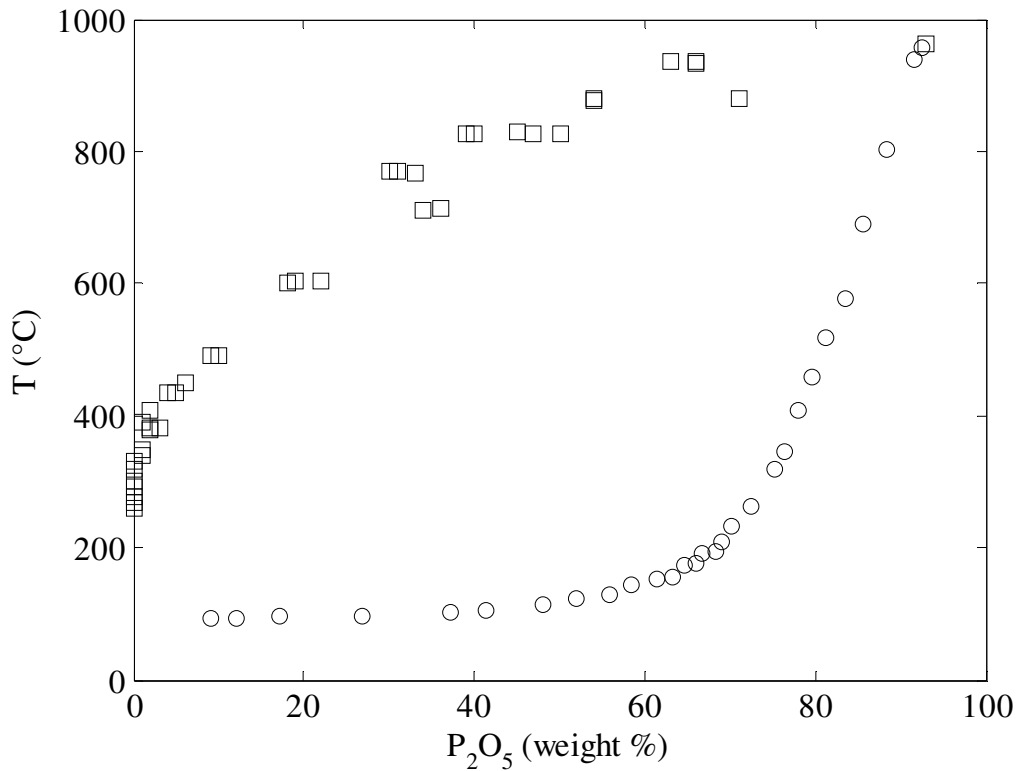Figure 2-2: Distribution of phosphoric acid as a function of P_2O_5 content (Jameson, 1959).

Figure 2-3: Vapour liquid equilibrium for liquid phosphoric acid (Brown & Whitt, 1952).

If the liquid phosphoric acid is however heated over an open flame at 200 °C time is not given for phase equilibrium to establish (shown in Figure 2-4).
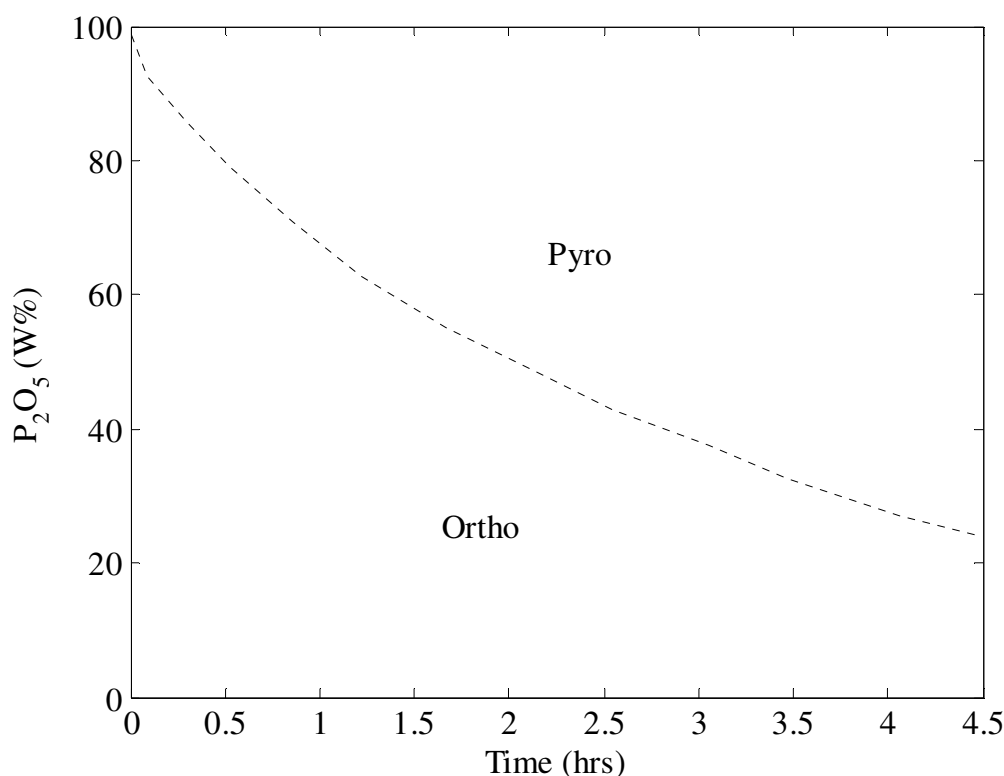

Figure 2-4: Acid distribution with time when heating liquid phosphoric acid over and open flame at 200 °C (Ohtsuka & Aomura, 1962).

If SPA, instead of liquid phosphoric acid, is rather heated in a muffle furnace it seems that the acid distribution evens out dependent on the type of support used, the distribution obtained for the heating of SPA composed of either Makkari kiezelguhr, Okayama kiezelguhr or Celite kiezelguhr is shown in Figure 2-5. If an equilibrium distribution was obtained at 200 °C the phosphoric acid strength would 70.5 W% P_2O_5, from the ortho - to pyro phosphoric distribution shown in Figure 2-5 it seems that the acid strength would equal 74.5%, 73% and 72% respectively. This stable acid distribution is quite close to what was measured by Brown and Whitt (1952) as the equilibrium distribution of the phosphoric acid which suggests that the free acid supported on the kiezelguhr support reaches a pseudo equilibrium distribution within the pores of the catalyst.
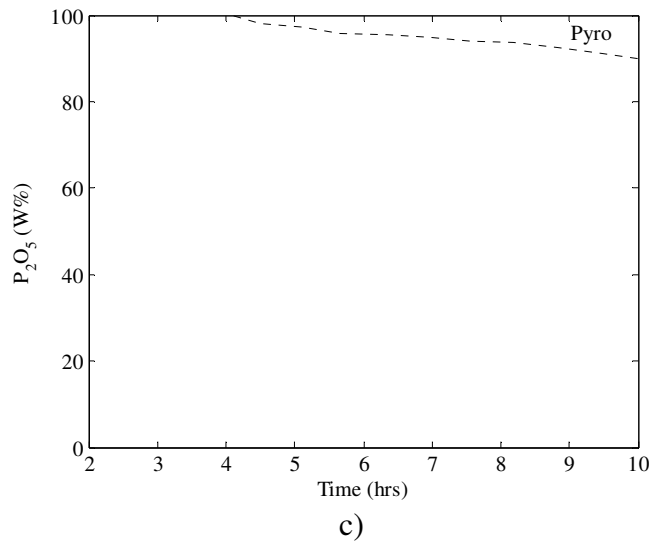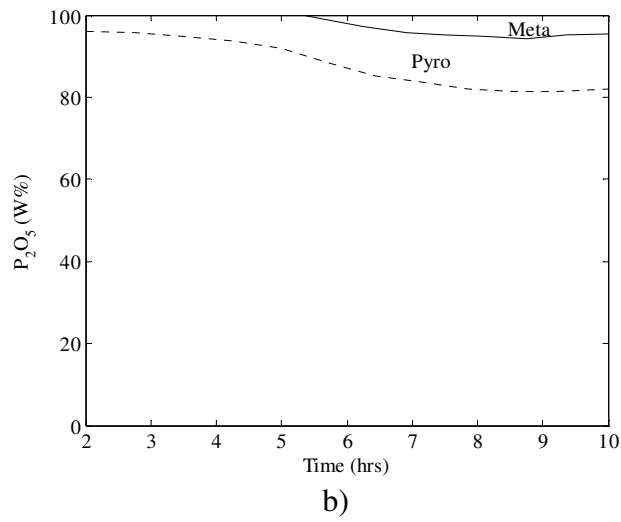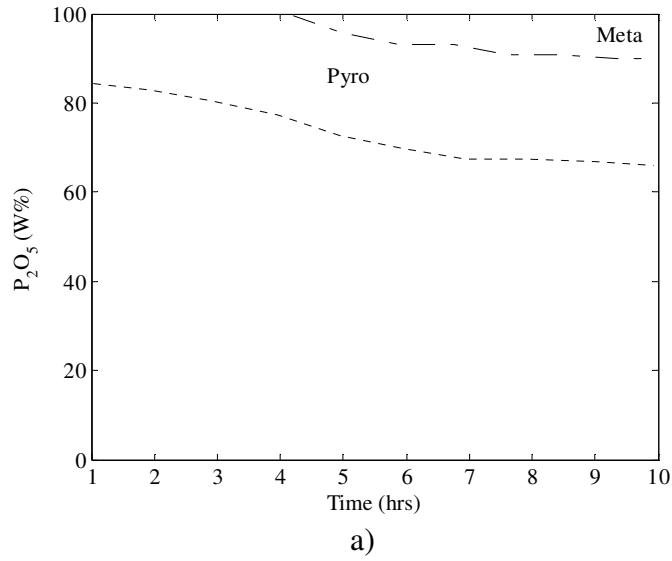
a)

b)

c)

Figure 2-5: Acid distribution over various kiezelguhr supports when heated in a muffle furnace at 200 °C

In short, the acid strength of the catalyst and the subsequent distribution of phosphoric acids are predominantly determined by the fraction of water present in the free acid layer. How the acid strength of the catalyst affects the activity of the catalyst is an altogether different matter.

2.5   Catalyst hydration

It is accepted that water inhibits the activity of solid acid catalysts (Okuhara, 2002). Generally this inhibition is due to the selective adsorption of water onto the acid site, effectively eliminating the active site from taking part in the reaction. Water is known to influence a phosphoric acid in various ways, *1)* blocking of active sites by selective adsorption onto the active sites, *2)* decreasing the activity of the catalyst by diluting the acid or *3)* improving the activity of the catalyst by liberation of free acid from the catalyst support (Makatun *et al.,* 1985).

For solid phosphoric acid, water is part of the free acid and will influence the distribution of phosphoric acid. As to how water will affect the reaction rate, remains indefinite. Work done by Skupińska (1991) indicates that the conversion of propene will increase with the adsorption of water onto the catalyst, whereas Cavani *et al.* (1993) state that an increased quantity of water in the feed significantly inhibits the oligomerisation rate of propene over SPA. The inhibition was found to be prominent only where the free acid content was larger than 20% (weight %), for free acid concentrations lower than 20%, the liberation of fixed phosphoric acid on the catalyst support (silicon phosphates) to the free acid layer occurs. This increases the total free acid concentration resulting in an increase in catalytic activity. According to Cavani *et al.* (1993) the inhibiting effect of increased hydration levels is believed to be twofold. Firstly, SPA is extremely hydrophilic, flooding the pores when excess water is present in the reaction mixture and restricting access to the catalytically active sites and secondly, by altering the phosphoric acid distribution (Figure 2-2). An increase in catalytic activity was also noted by Langois and Walkey (1952) when using a dry feed to the reactor for phosphoric acid impregnated on quarts.

Some water however needs to be present for catalytic activity. Deeter (1950) indicated that initial activity of a *properly* hydrated catalyst to be higher than that of a under hydrated catalyst. Therefore to control the activity of the catalyst both temperature and water need to be controlled.

Water does not only influence the activity of the catalyst but can also effect the life time, Weinert and Egloff (1948) stipulated that water is needed in the reactor feed to prevent the catalyst from becoming dehydrated. Over hydration of the catalyst results in the softening of

the catalyst, leading to the plugging of the reactor bed, whereas under hydration will result in coke formation. Over hydration will also result in leaching phosphoric acid from the catalyst which will result in corrosion of the reactors (Egloff and Welnert, 1951), further emphasizing the importance of hydration control over the reactor.

For cases where oxygenates are present in the reactor feed, as is the case for feed produced from high-temperature Fischer-Tropsch, it has been shown that the oligomerisation is significantly inhibited. This is especially true for the oligomerisation of the C_5-C_6 cut which contains a large fraction of oxygenates (3 weight %). When oligomerising 1-hexene the addition of various oxygenates to the reaction mixture inhibits the oligomerisation as well as the rate of isomerisation over SPA (De Klerk *et al.*, 2007). The inhibition of the oligomerisation rate is largely attributed to the formation of water which form from the dehydration of oxygenates. This decreases the acid strength of the free acid, resulting in the decreased activity of the catalyst (Mashapa and De Klerk, 2007).

Prinsloo (2006) showed an increased propensity toward the production of distillate range products from the oligomerisation of propene with an increase in the acid strength of the free acid. A maximum in the distillate selectivity occurs at an acid strength of 108% H_3PO_4 (78% P_2O_5, Figure 2-2) where the pyro phosphoric acid is at a maximum. Thereafter a drop in the diesel selectivity was observed. The propylene conversion was also seen to increase as the acid strength increased. The maximum observed in the selectivity, at an acid strength of 108% H_3PO_4, was not seen for conversion. The conversion increased up to 108% H_3PO_4 and then flattened out. The flattening out of activity at higher acid strengths was also noted by Ohtsuka and Aomura (1962), which attributed this to the formation of meta phosphoric acids (highly condensed phosphoric acids). This suggests that pyrophosphoric acid mostly controls the activity of phosphoric acid.

However, it is not so easy to determine the phosphoric acid distribution of the free acid supported on the kiezelguhr, as given by Jameson (1959) for liquid phosphoric acid (Figure 2-2), since the acid is supported on the catalyst and extracting the liquid acid without altering the acid distribution is difficult (Cavani *et al.*, 1993).

The quantity of free acid is usually determined by the addition of an excess of water to the catalyst, which results in the leaching of the free acid from the catalyst support. If the contact time is too long, fixed acid (silicon phosphates) will also desorb, giving an inaccurate representation of the free acid fraction (Cavani *et al.*, 1993; Coetzee *et al.*, 2006). The titration of the water liquor will indicate the quantity of hydronium ions due to the complete hydrolysis of stronger acids to ortho phosphoric acid (Equations 2-6 and 2-7). Therefore the

titration will only indicate the quantity of ortho phosphoric acid present in the free acid, not the form of the phosphoric acid (ortho/pyro).

Zhirong *et al.* (2000) used ion chromatography to determine the distribution of ortho and pyro phosphoric acid in the free acid. In the end, these researchers could not report any definite trend between the total quantity of free acid and the catalytic activity towards propene oligomerisation, but it was shown that with an increase in the pyro phosphoric acid content (i.e. less water), the conversion of propylene increased (Figure 2-6) further advocating increased activity with increased acid strength.

De Klerk *et al.* (2006) investigated the effect of operating conditions on the oligomerisation of butene over liquid phosphoric acid. The investigation focused on gaining an idea of the influence of acid strength and temperature on the degree of branching of the C_8 olefins as well as the gasoline-to-distillate ratio (gasoline was taken as all compounds boiling lighter than 175 °C). It was found that as acid strength and temperature decreased, the degree of branching of the product as well as the gasoline production increased, (see Figure 2-7 *a)*, which suggest that the optimum operating condition for gasoline production would be at a high hydration (low acidity) of the catalyst and a low temperatures.

It was suggested that both high temperature and high acid strength would result in a greater likelihood of the cracking of branched product, which would decrease the gasoline quality (De Klerk, 2006b). With the increased distillate ratio at higher acid strengths and higher temperatures, Figure 2-7 *b)*, the increased activity of the catalyst results in the formation of more trimer product (C_{12}s, boiling point 214 °C). Therefore the decreased gasoline quality at these conditions could be due to the greater reactivity of the branched C_8 olefins, selectively reacting with shorter chain olefins toward the formation of diesel range products.
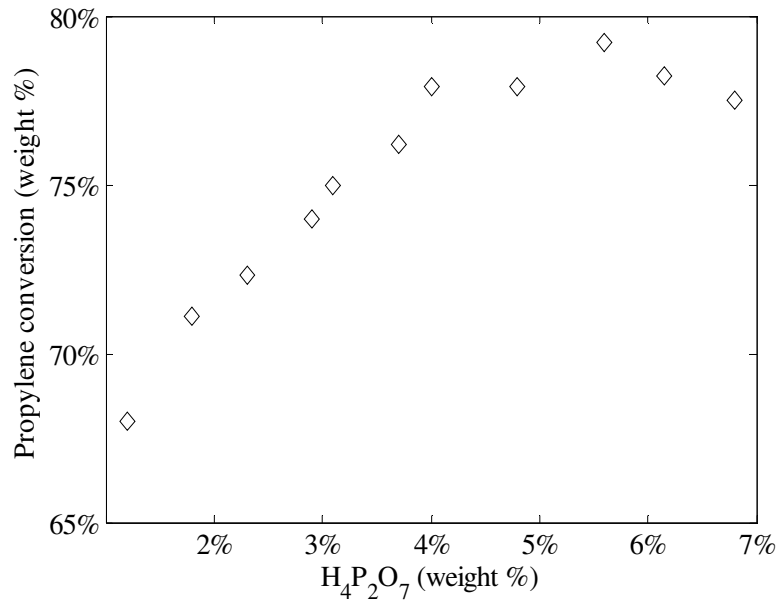
Figure 2-6: The effect of $H_4P_2O_7$ (wt %) on the conversion of propylene (Zhirong *et al.*, 2000).
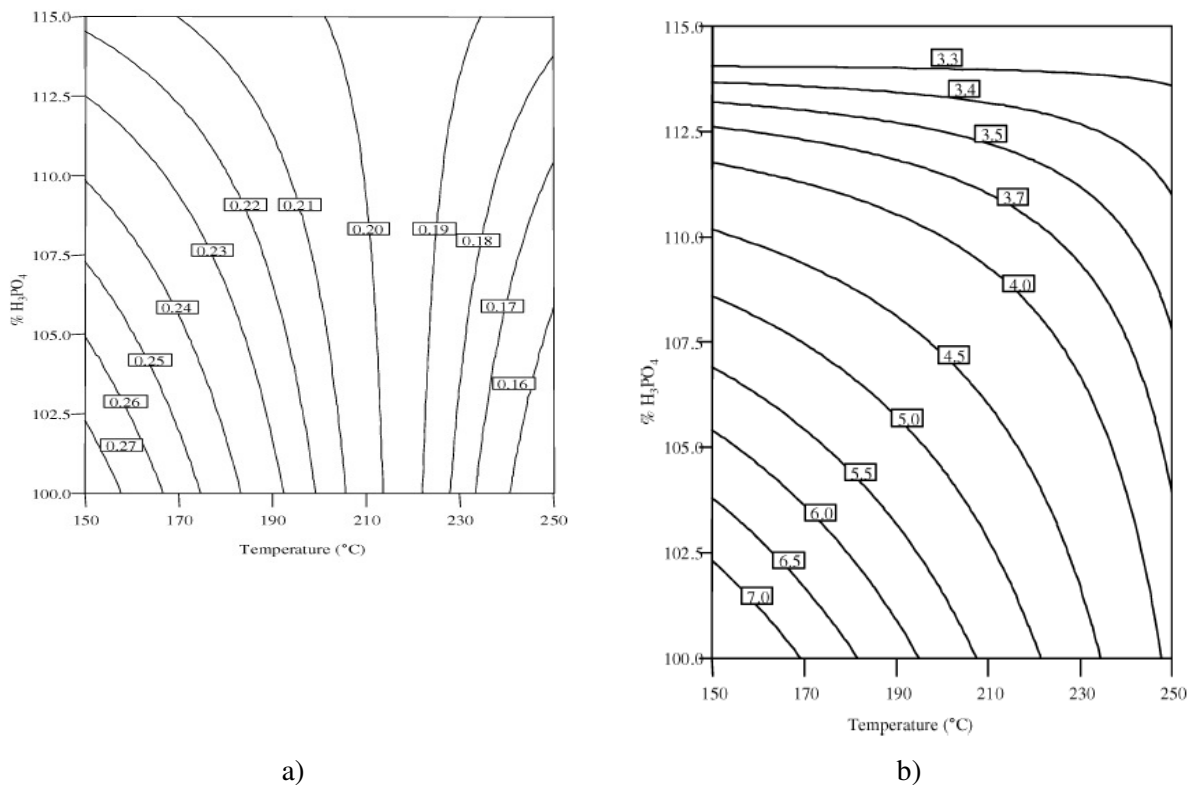

a)   b)

Figure 2-7: Effect of acid strength and temperature on *a)* degree of branching of C_8 olefins and *b)* gasoline-to-distillate ratio for C_4 oligomerisation, for a constant residence time, over liquid phosphoric acid (De Klerk *et al.*, 2006).

2-18

The increase in activity with increase in acid strength is corroborated in one of the first articles studying the effect of acid strength on the rate of oligomerisation of propene using liquid phosphoric acid as catalyst. Bethea & Karchmer (1956) approximated the rate of oligomerisation of propylene for various acid strengths of the catalyst. When the acid strength was increased, the first order rate constant increased exponentially with the increase in acid strength, Figure 2-8. This increase in the reaction rate was also seen by Monroe and Gilliland (1938) for the oligomerisation of propene over dilute liquid phosphoric acid, where the reaction rate was found to be proportional to the square of the propene partial pressure, the volume of acid and the acid strength of the catalyst.
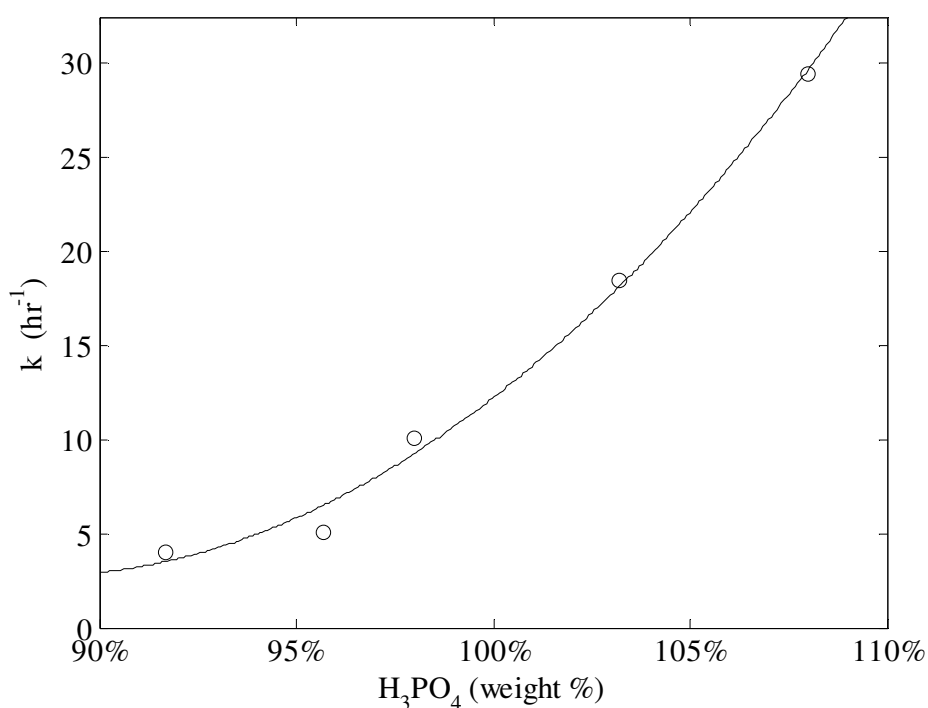

Figure 2-8: Effect of acid strength on the rate constant of Bethea & Karchmer (1956).

Therefore, the reaction rate over phosphoric acid is exponentially dependent on both the reaction temperature and the acid strength of the phosphoric acid, Figure 2-9. From the Arrhenius trend it seems that the activation energy also increases with an increase in acid strength. No attempt was made to integrate the acid strength effect with the rate constant or to relate the conversion of propylene to the resulting product. It was noted, however, that as the acid strength increased, the selectivity of the oligomerisation changed from predominantly trimerisation (C_9) to tetramerisation (C_{12}). At an acid strength of 92% H_3PO_4 the ratio of

C$_9$:C$_{12}$ was 2.33:1 whereas at an acid strength of 109% H$_3$PO$_4$ the ratio changed to 1:1.56, as would be expected for a sequential reaction at increased activity of the catalyst.
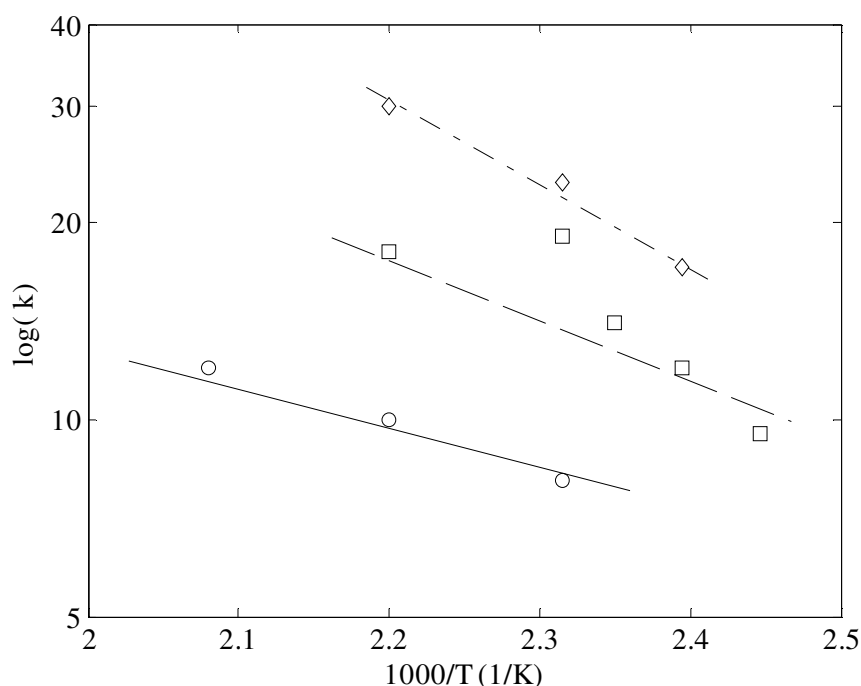

Figure 2-9: Effect of acid strength on the rate constant, $\circ$ – 98% H$_3$PO$_4$, $\square$ – 103% H$_3$PO$_4$, $\lozenge$ - 109% H$_3$PO$_4$ (Bethea & Karchmer , 1956).

As to how quickly the phosphoric acid stabilizes upon the introduction of water to the reaction system, Vinnik and Obraztsov (1983) showed that the introduction of water to the reactor reduces the catalytic activity but recovers to initial activity within minutes.

Fairly little work has been done in the literature on modelling the effect of acid strength on the reaction rate. The only attempt that could be found was in the doctoral thesis of McClean (1987) while modelling the rate of oligomerisation of C$_3$ and C$_4$ olefins. It was noted that when there was an increase in acid strength, the rate of oligomerisation increased. This was compensated for by adapting the rate constant as shown in Equation 2-9. However, when the model was applied to experimental data to characterise the influence of acid strength, negative activation energies ensued.

$$k_x = k_o e^{-\frac{E}{T}}.\left[\%H_3PO_4/100\right]^y \qquad\qquad 2\text{-}9$$

Conflicting arguments are present in the literature concerning the effect of water on the reaction rate and the product selectivities. Mostly the literature have focused on drawing trends based on hydration variations at a constant space velocity without taking the reaction progression into account. A kinetic evaluation of the effect of hydration would be instrumental to closing the loop to the effect of hydration on oligomerisation over SPA.

2.6   Reaction mechanism/network

When modelling the reaction kinetics for the oligomerisation of an olefin, various routes or products are plausible. The reaction mechanism/network defines these routes a reagent can follow from possible intermediates to the formation of the products, but does not delve into rate difference between these routes. For kinetic modelling the rate difference between these intermediates are critical toward predicting the formation of the desired product. This is especially true if the feed contains the different intermediates present in the reaction network.

This is true for a feed present in a petrochemical refinery. Even though mostly olefins and paraffins are present in the feed, a variety of reactions can occur in series and/or parallel, namely double bond shift, skeletal isomerisation, cracking, disproportionation and cyclisation, Figure 2-10. Since each of these reactions is important to the quality of the produced fuel, choosing the catalyst and operating conditions is critical. Over SPA all of the previously mentioned reactions occur. Cracking is limited to olefins with a carbon number greater than seven at temperatures below 275 °C (De Klerk, 2005b), this is quite important for this investigation since when oligomerising 1-hexene cracking of the feed can be excluded from the reaction scheme. Below 200 °C only acyclic mono olefins are evident (De Klerk, 2006b) with paraffin formation becoming more likely bove 300 °C (Skupińska, 1991). The scope of this study covers only isomerisation, oligomerisation and cracking of the olefin feed.
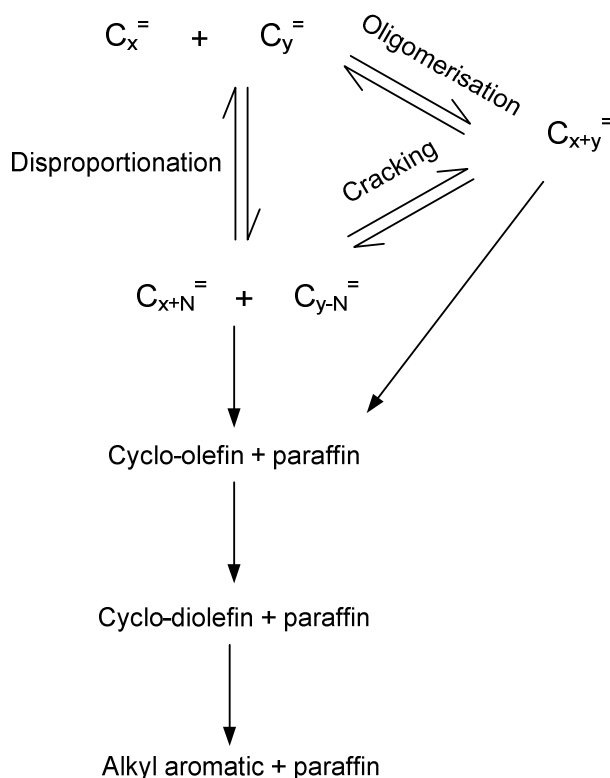
Figure 2-10: Various reactions that can occur during the oligomerisation of two olefins (Quan *et al.*, 1988).

One of the differences in the oligomerisation of olefins over phosphoric acid, is the difference in the reaction mechanism. Usually oligomerisation is assumed to occur through the classic carbocation mechanism, whereas for phosphoric acid oligomerisation occurs through a phosphoric acid ester intermediate.

2.6.1 Classic carbocation mechanism

When an acid catalyst is used for the oligomerisation of olefins, it is usually assumed that a carbocation mechanism prevails (Figure 2-11). The stability of the carbocation intermediate dictates the differences in reactivity, methyl and hydrogen migration and product selectivity. With increased substitution, the carbocation intermediate becomes more stable and therefore the reactivity increases (McMurry, 2000).
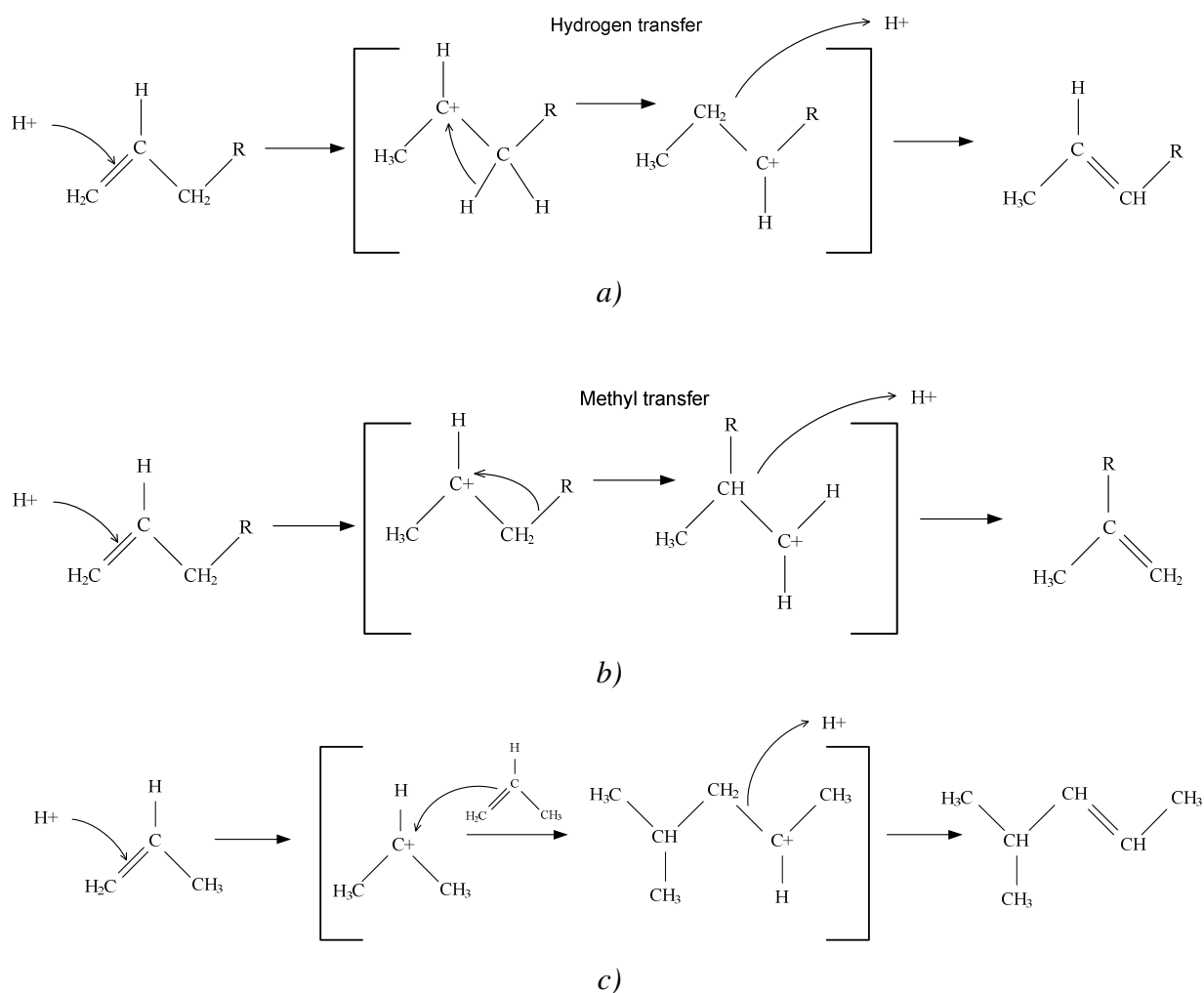
Figure 2-11: Classic oligomerisation carbocation mechanism for *a)* double bond isomerisation, *b)* skeletal isomerisation and *c)* oligomerisation.

2.6.2 Phosphoric acid ester mechanism

The formation of an ester intermediate is not limited to phosphoric acid, and has also been seen for the oligomerisation of alkenes over sulphuric acid (Schmerling and Ipatieff, 1950). Several authors in the literature propose that oligomerisation over SPA occurs through an ester intermediate (Ipatieff, 1935; Schmerling and Ipatieff, 1950; De Klerk, 2006b; Mashapa and De Klerk, 2007). The ester intermediate was first seen by Ipatieff (1935) who heated liquid phosphoric acid and an olefin in an autoclave at 10 atm. At low temperatures a single layer was present in the autoclave, this layer was found to be the phosphoric acid ester. When the mixture was heated the liquid dissolved into two layers (phosphoric acid and the olefin). Ethyl phosphoric acid ester was found to be stable up to 200 °C, whereas propyl phosphoric

acid ester was stable up to 125 °C. This suggests a temperature barrier that has to be overcome to destabilise the phosphoric acid ester before the oligomerisation reaction can occur (De Klerk *et al.,* 2004) and that the stability of the phosphoric acid ester drops with an increase in the chain length of the olefin. The stability of the ester is also dependent on the degree of branching of the olefin, owing to the increased rate of oligomerisation of branched octenes (De Klerk, 2006b).

Before oligomerisation can take place an ester is formed between the olefin and the liquid phosphoric acid, Figure 2-12 (Ipatieff, 1935).
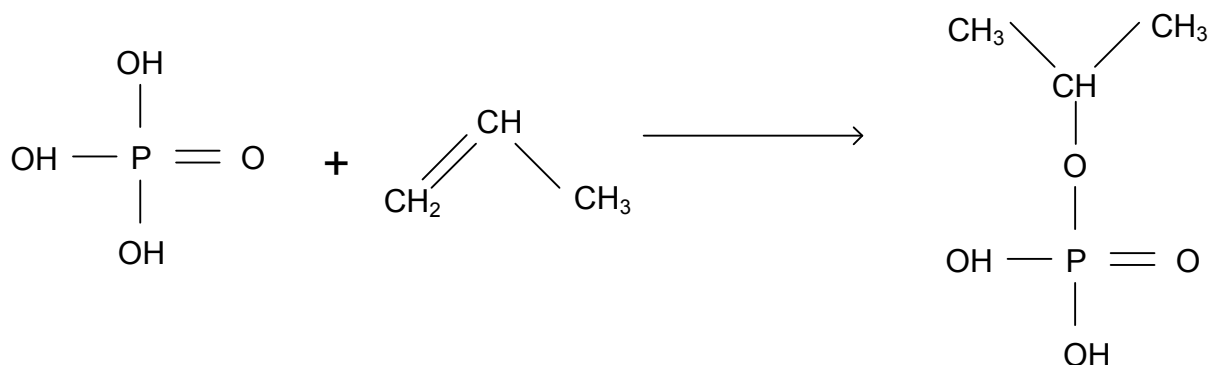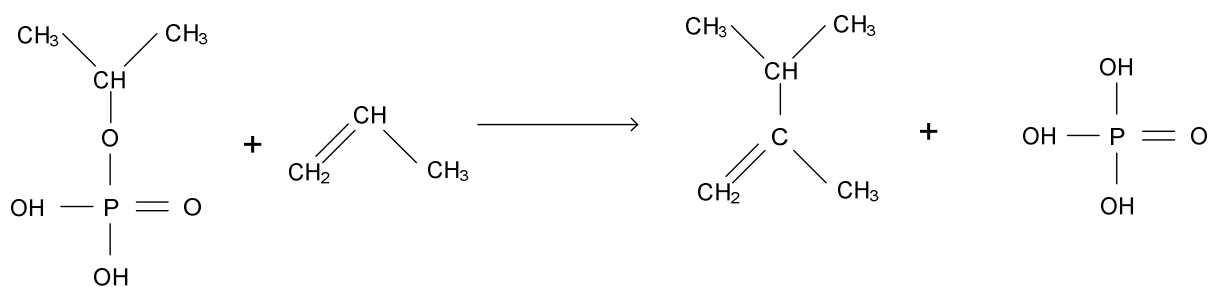

Figure 2-12: Phosphoric acid mechanism (Ipatieff, 1935)

Oligomerisation can then take place by either *1)* an ester reacting with an olefin, Figure 2-13 *a)* or *2)* by two esters reacting with each other to form a hexene isomer, Figure 2-13 *b)* (Schmerling and Ipatieff, 1950).
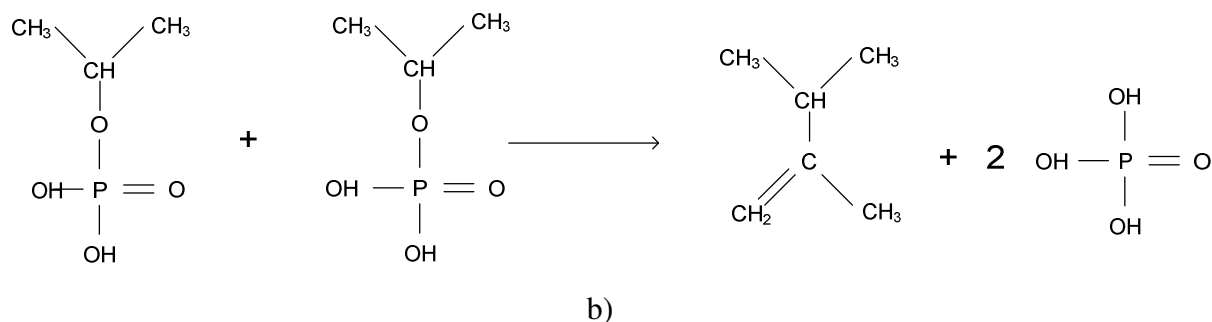

a)

b)

Figure 2-13: The ester mechanism for a) one olefin reacting with an olefin or b) two esters dimerising.

Farkas and Farkas (1942) proposed that the formation of the phosphoric acid intermediate with the olefin by taking up hydrogen or by donating one hydrogen atom (Figure 2-14). This describes the route the molecule follows to the product as well as the stability of the intermediate, which could result in different activation energies dependent on the formed intermediate.
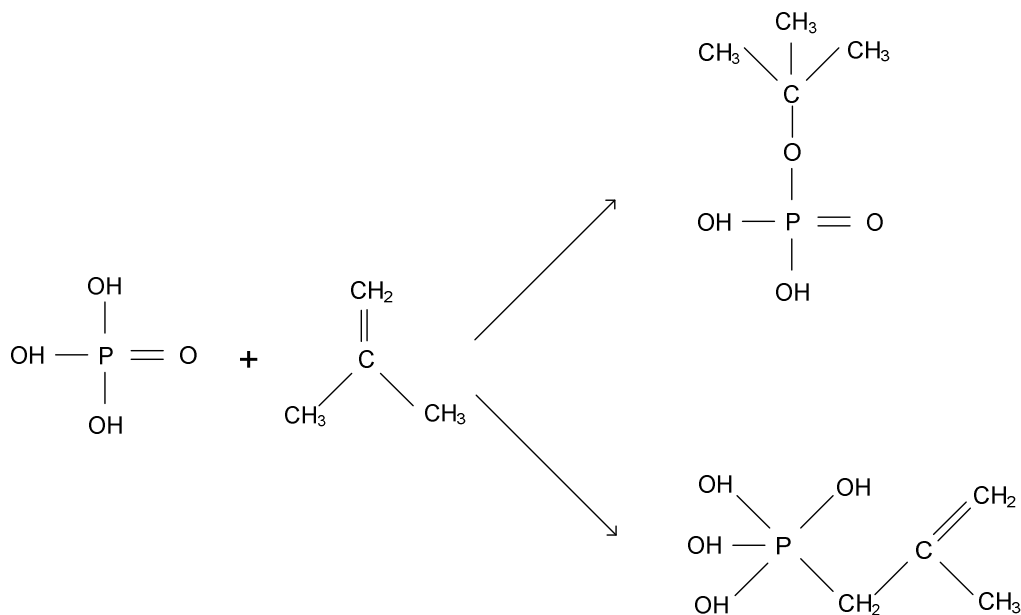

Figure 2-14: Reaction mechanism as proposed by Farkas and Farkas (1942).

Double bond shift and skeletal isomerisation both occur through the phosphoric acid intermediate, Figure 2-15 (De Klerk, 2006b). The presence of iso-butene and highly branched oligomerised product, for the oligomerisation of 1-butene at low temperatures (130 °C), indicates that SPA is adept at the isomerisation of olefins. SPA has also been shown to be capable of the skeletal isomerisation of longer chain olefins with the isomerisation of 1-hexene at elevated temperatures, 285-500 °C and atmospheric pressure (Hay et $al.$, 1945).

This ability of SPA to isomerise olefins, even at low temperatures, is advantageous to the production of gasoline, due to the increased RON value of highly branched paraffins.
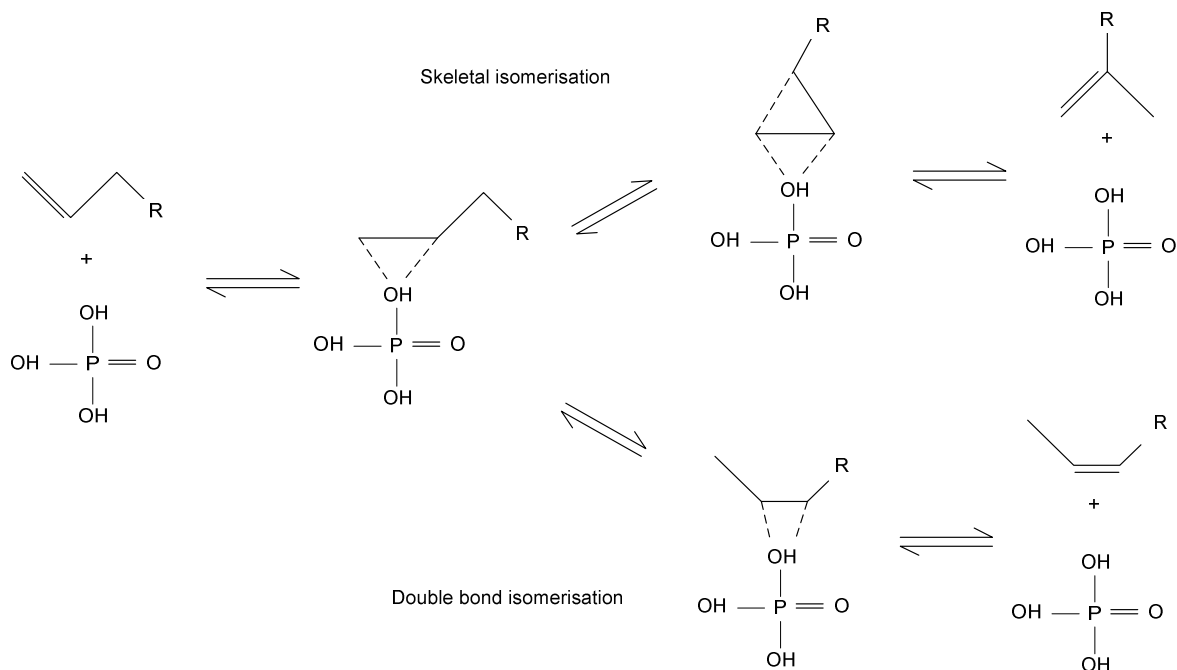

Figure 2-15: Phosphoric acid ester mechanism for skeletal and double bond isomerisation.

Since double bond -, skeletal isomerisation and oligomerisation can occur through both the carbocation and the ester mechanism the reaction route followed for both mechanisms are similar. The difference between the two would be the relative activation energies needed to model the reaction rate, since no previous kinetic parameters are available for 1-hexene oligomerisation over either catalyst no comparison is possible for the activation energies.

2.7   Kinetic modelling of oligomerisation over acid catalyst

Kinetic modelling of the reaction rate over SPA focused on the rate of oligomerisation of short chain olefins, these include the work done by Paynter & Schuette (1971), Friedman & Pinder (1971), Cao *et al.* (1988) and the doctoral thesis of McClean (1987). For other acid catalysts the literature is more prominent (Alcántara *et al.*, 2000; Honkela *et al.*, 2003; Honkela *et al.*; 2004 Cruz *et al.*, 2007;).

The oligomerisation of short chain olefins over and acid catalyst is mostly with the intent of producing petrol, therefore precautions have been taken to limit the extent of the oligomerisation, especially for the selective production of highly isomerised octenes from iso-butene. Over sulphonic cation exchange resins, the oligomerisation of iso-butene can run

away easily to form trimer and tetramer product at mild operating conditions, 100 °C and 94 kPa (Alcántara *et al.*, 2000). Although oligomerisation over a cation exchange resins follows the classical Brønsted mechanism, the increased reaction rate noticed for iso-butene with respect to the rate seen for linear butenes also holds true for SPA (McClean, 1987). Therefore the higher reactivity of skeletal isomers is valid for both traditional Brønsted acids and SPA. For cation exchange resins, one method which has been used to limit the extent of the oligomerisation is the addition of alcohols to the reactor feed. This limits the oligomerisation to a gasoline-range product and the formation of ethers which is beneficial to the octane of the resulting fuel (Di Girolamo *et al.*, 1997; Cruz *et al.*, 2007; Honkela *et al.*, 2003). The addition of ethers to the gasoline pool has been met with some concern, however, due to the contamination of ground water. For this reason, oxygenates that do not participate in the oligomerisation reaction have been used to limit the extent of oligomerisation, such as tertiary butyl alcohol (TBA) (Honkela *et al.*, 2003; Honkela *et al.*, 2004).

The use of oxygenate compounds as well as branched short chain olefins decreases the amount of possible products by negating the possibility of isomerisation. It is necessary to account for the differences in the adsorption selectivity between the oxygenates and olefins to adequately model the reaction rate. This is done by applying Langmuir-Hinshelwood adsorption to the reaction kinetics, as shown in Equation 2-10 for the dimerisation of iso-butene (IB).

$$r_{Dimerisation} = \frac{k_{Dimerisation} K_{IB}^2 \alpha_{IB}^2}{\left(K_{IB} \alpha_{IB} + K_{ITBA} \alpha_{TBA} + K_{Dimer} \alpha_{Dimer} + K_{Trimer} \alpha_{Trimer} \right)^2} \quad \text{2-10}$$

The reaction network, with regard to the amount of possible dimer products, grows considerably for the oligomerisation of a C_5 olefin, Figure 2-16. To simplify the reaction network, lumping of the products and reagents ensues. This simplifies the modelling of the reaction network for C_5 oligomerisation. If however a more thorough depiction of the reaction products is needed, especially when the fuel properties are highly sensitive to the composition of the product, a more complicated reaction network will result. Such is the case when modelling the rate of oligomerisation for methyl-butene, where 11 reaction constants are needed to describe the reaction network (Cruz *et al.*, 2007). Validating each of the kinetic parameters would require a great deal of experimental work with a detailed analysis of the product, which is not always a viable option. For instance, if the reaction network was rather

completed for 1-pentene, skeletal isomerisation would need to be incorporated in the reaction route, as well as the dimerisation and co-dimerisation of all the pentene isomers. This would result in a dramatic increase of the reaction network depicted below.
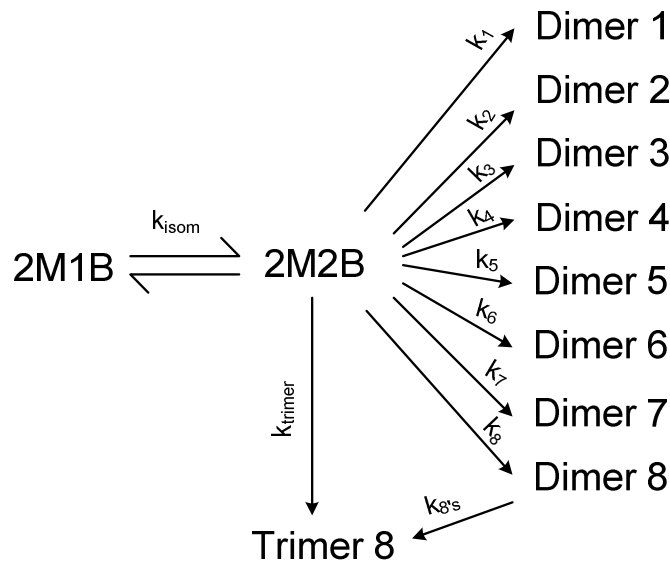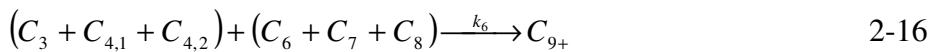

Figure 2-16: Reaction network for the oligomerisation of 2-methyl-1-butene (2M1B).

Although the increased reactivity of iso-butenes (and selectivity to highly branched petrol) have been noted for SPA oligomerisation using a FT derived feed (De Klerk *et al.*, 2004), the addition of oxygenates to limit the reaction rate of iso-butene has not been investigated due to the negative impact of oxygenates on the reaction rate over SPA (De Klerk *et al.*, 2007). Although using TBA for oligomerisation over SPA to limit the reaction rate and increase the selectivity to high RON petrol could be useful if a high fraction of iso-butene is present in the feed.

Considering that the oligomerisation of short chain olefins have been practised for some time over SPA, fairly little has been done to model the kinetics involved in the reaction. The models have also relied extensively on the lumping of species to minimise the number of parameters needed in the kinetic model. In 1971 the first attempts at modelling the oligomerisation of an olefin mixture over SPA were made, firstly by Friedman & Pinder (1971) and secondly by Paynter & Schuette (1971). Friedman & Pinder (1971) used a second order kinetic model to approximate the rate at which propene disappeared from the reaction mixture. Only an apparent rate constant was modelled as internal mass transfer was evident.
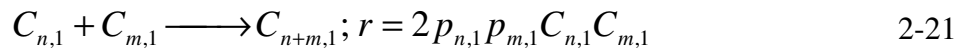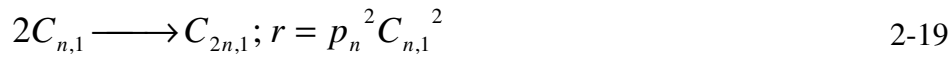
Paynter & Schuette (1971) made the first attempt at using kinetics to describe the resulting product distribution from the oligomerisation of propenes and n-butenes over SPA, as can be seen in Equations 2-11 to 2-18. Due to selectivity differences between 1-butene and 2-butene,

the reactivity of the two isomers was split, but the formation of olefins larger than C_9 was grouped under a lumped rate constant. Paynter & Schuette (1971) gathered their experimental data at mild operating conditions (115°C), this ensured that only oligomerisation needed to be modelled since at these low temperatures cracking did not occur. The reactivity difference with increased chain length was determined to be $k_2 > k_1 > k_4 > k_3 > k_5$. This suggests that the co-dimerisation of C_3 and C_4 olefins occur the fastest, followed by C_3 oligomerisation and then by C_4 oligomerisation.

$$2\,C_3 \xrightarrow{\ k_1\ } C_6 \qquad\qquad\qquad\qquad\qquad\qquad \text{2-11}$$

$$C_3 + C_{4,1} \xrightarrow{\ k_2\ } C_7 \qquad\qquad\qquad\qquad\qquad\qquad \text{2-12}$$

$$C_3 + C_{4,2} \xrightarrow{\ k_3\ } C_7 \qquad\qquad\qquad\qquad\qquad\qquad \text{2-13}$$

$$2\,C_{4,1} \xrightarrow{\ k_4\ } C_8 \qquad\qquad\qquad\qquad\qquad\qquad \text{2-14}$$

$$2\,C_{4,2} \xrightarrow{\ k_5\ } C_8 \qquad\qquad\qquad\qquad\qquad\qquad \text{2-15}$$

$$\left(C_3 + C_{4,1} + C_{4,2}\right) + \left(C_6 + C_7 + C_8\right) \xrightarrow{\ k_6\ } C_{9+} \qquad\qquad \text{2-16}$$

$$C_{4,1} \xleftrightarrow{\ k_7\ } C_{4,2} \qquad\qquad\qquad\qquad\qquad\qquad \text{2-17}$$

$$3\,C_3 \xrightarrow{\ k_8\ } C_{9+} \qquad\qquad\qquad\qquad\qquad\qquad \text{2-18}$$

Cao *et al.* (1988) expanded on the kinetic model proposed by Paynter & Schuette (1971) who lumped all olefins larger than C_9 under the same reaction constant. For this reason a limited perspective of the product can be formulated from the reaction network/model. Coa *et al.* (1988) proposed a kinetic model that could differentiate between the product chain lengths. For the sake of simplicity, the reagents were lumped based on the chain length with an added parameter for the isomerisation of the olefin to a non-reactive olefin (irreversibly). It was also assumed that the rate of isomeriserisation was independent of the chain length of

the olefin that was isomerised. Due to the low temperature of the investigation, cracking could still be ignored. A kinetic parameter ρ_n was used to approximate the reactivity of a lumped olefin chain length. The reactivity between two olefins was then taken as the product of the individual reactivities ($\rho_n \cdot \rho_m$). The resulting kinetic expression used is shown in Equations 2-19 to 2-21.

$$2C_{n,1} \longrightarrow C_{2n,1}; r = p_n^2 C_{n,1}^2 \qquad \text{2-19}$$

$$C_{n,1} \longrightarrow C_n; r = k_{iso} C_{n,1} \qquad \text{2-20}$$

$$C_{n,1} + C_{m,1} \longrightarrow C_{n+m,1}; r = 2 p_{n,1} p_{m,1} C_{n,1} C_{m,1} \qquad \text{2-21}$$

Only olefins up to C_7 were taken as being likely to oligomerise with the maximum chain length formed limited to C_{14}. From the kinetic modelling, the reactivity of olefins was determined to be: $\rho_6 > \rho_3 > \rho_{4,1} > \rho_7 > \rho_{4,2}$. This is similar to the reactivity sequence given by Paynter & Schuette (1971). The high reactivity of C_6 olefins is questionable, since for the oligomerisation of C_3s over SPA, a high selectivity results in C_9 and C_{12} olefins (Table 2-4). If only dimerisation and co-dimerisation propene are assumed, the optimisation of the kinetic fit would inevitably result in a high reactivity of C_6 olefins, especially in the case of the reaction mechanism proposed by Coa *et al.* (1988). Furthermore the reactivity of C_6 was not validated by spiking hexene into the reaction mixture to investigate the reactivity of the olefin. Another possibility is the one-step trimerisation of C_3 to C_9, but this was not investigated by Coa *et al.*(1988).

Table 2-4: Product spectrum for varied conversion of pure propene from McClean (1987).

Conversion of propene	5%	13.7%	32.0%
Product concentration (mol.l^{-1} $\times 10^3$)			
Butene	0.0	0.0	0.0
Pentenes	0.0	0.0	0.0
Hexenes	0.3	2.0	4.7
Heptenes	0.0	0.2	0.7
Octenes	0.0	0.4	1.3
Nonenes	3.7	12.1	30.2
Decenes	0.1	0.3	1.3
Un-decenes	0.2	0.6	1.6
Do-decenes	1.5	3.6	11.0
> Do-decene	0.1	0.3	1.1

One investigation which used SPA and did look at the oligomerisation of hexene, was that of McClean (1987). The work focused on the oligomerisation of butene and propene and, to gain an understanding of the reaction mechanism over SPA, hexene was also oligomerised. The resulting reaction network is shown in Figure 2-17. Cracking was only observed for olefins longer than C_8. No cracking products shorter than C_4 olefins was observed.

A significant difference in reactivity was observed for the oligomerisation of butene and iso-butene, but no difference in reactivity was evident for the oligomerisation of different hexene isomers. The goal of the thesis of McClean (1987) was not to model the reaction rate of 1-hexene, but rather to model the reaction rate for C_3 and C_4 oligomerisation (hexene was used as to understand the reaction progression of propene). Although a rate difference was apparent for iso-butene this was not captured in the reaction model of butene oligomerisation. This could be a critical misrepresentation of the reaction mechanism since the product spectrum from butene oligomerisation (Bekker and Prinsloo, 2009) shows a significant fraction of branching in the product. As such isomerisation of butene is critical towards the reaction route followed and ultimately towards predicting the product quality. McClean (1987) modelled the reaction kinetics for the oligomerisation of pure propene and butene, with the dimerisation and co-dimerisation of multiples of propene and butene; cracked products formed from the cracking of C_{12} olefins were lumped. The resulting optimisation of

the kinetic parameters resulted in negative activation energies, leaving questions about the empirical nature of the model.
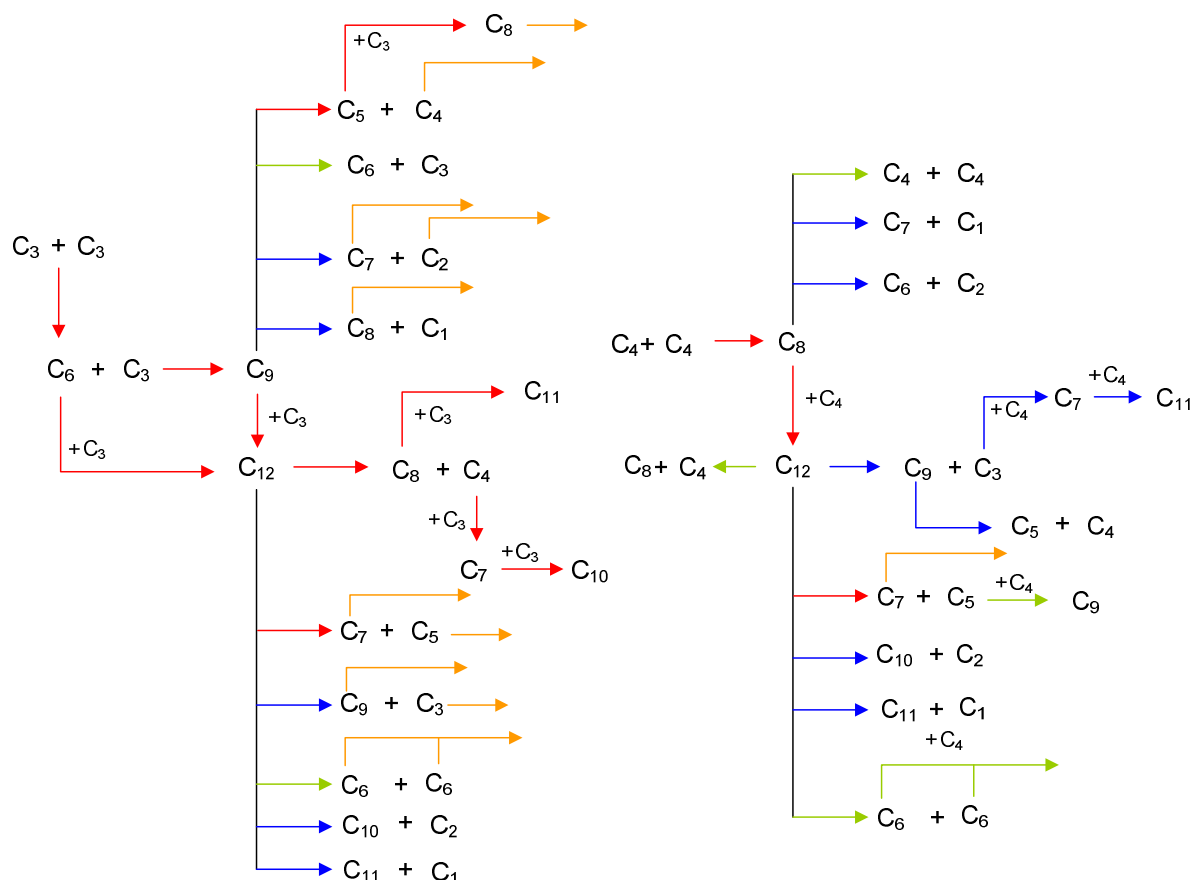

Figure 2-17: Reaction mechanism for McClean (1987). Reaction significance: → significant occurrence, → insignificant occurrence, → unknown occurrence, → normal route.

Modelling the oligomerisation over SPA is simplified by lumping all the carbon isomers under the same species (e.g. C_4 olefins would include 1-butene and iso-butene). This simplifies the possible reaction schemes by removing isomerisation and changing the varied amount of isomerised product to a single carbon number. This assumption would be adequate if the reactivates of varied isomers remained constant, which unfortunately is not always the case.

2.8   Closing remarks

Oligomerisation over SPA has been around since 1935 and extensive work has been done with various feeds over the catalyst. Many of these observations link directly to the reaction rate noticed over SPA. Firstly it has been shown that branched olefins of the same carbon length is more reactive than their linear counterparts, secondly the increased activity of the

catalyst has also been noticed where the acids strength of the catalyst has been increased. Although the articles listing these effects on the reaction rate over SPA are numerous, little has been done to include these effects in predicting the reaction rate over SPA. Where the reaction rate has been modelled (Paynter & Schuette, 1971; McClean, 1987; Coa *et al.*, 1988) these aspects of the oligomerisation over SPA has not been included in the proposed reaction kinetics. Not only has the increased reactivity of branched olefins been ignored when modelling the reaction rate, the propensity of SPA to skeletal isomerisation has also not been included in modelling the reaction progression over SPA.

This thesis investigates the oligomerisation of 1-hexene with regard to the reaction progression from 1-hexene to oligomerised and cracked products over a wide temperature range. Since it has been shown that branched olefins have a higher reactivity over the catalyst, the current research will attempt to incorporate the reactivity differences of linear (1-hexene) and branched olefins (2,3-dimethyl-2-butene) together with skeletal isomerisation in the proposed kinetic model (Chapter 3). The link between activity and acid strength on the reaction rate will be investigated in Chapter 4 by altering the acid content of the catalyst as well as the addition of water to the reaction mixture.