

Kinetic model for the dimerisation of 1-hexene over a solid phosphoric acid catalyst

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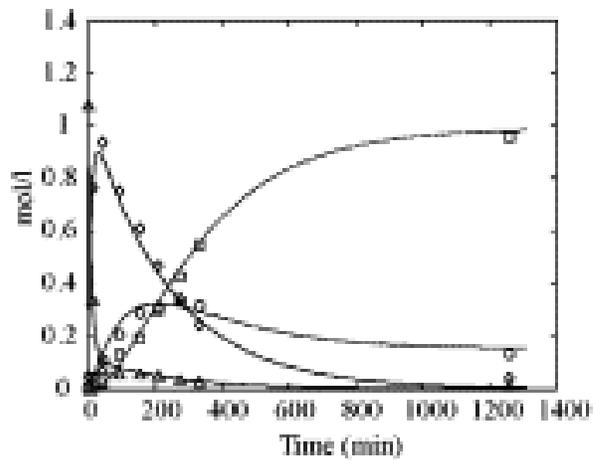
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Abstract

Batch kinetic experiments at 150 °C, 200 °C and 250 °C showed that the reaction can be modeled with a three step sequential reaction scheme. This involves firstly linear isomerisation of 1-hexene followed by skeletal isomerisation and finally dimerisation and cracking. The first and last steps in the sequence are modeled as reversible reactions. When first order reaction kinetics is assumed for each of the reactions, the model gave a very good representation of the experimental data. In order to test the validity of the series pathway hypothesis, the reaction was repeated with a skeletal hexene isomer – 2,3-dimethyl-2-butene (DMB) – as reactant. Although the rate and equilibrium constants for the third reaction step as obtained from the 1-hexene conversion data gave a good prediction of the DMB conversion at 200 °C and 250 °C, it failed to predict the reaction rate at 150 °C. This suggests that a different reaction pathway – where linear hexene isomers are directly converted to dimer product – becomes more significant at lower temperatures. The relatively high activation energy of the linear to skeletal hexene reaction may be to blame for this observation. However, this needs to be confirmed by further experimental work. The same equilibrium conversions of both 1-hexene and DMB were observed at all three temperatures investigated—suggesting that the equilibrium conversion is independent of the type of hexene isomer in the reaction mixture.

Graphical abstract

A sequential reaction pathway is proposed for this reaction. The three reaction steps included in the model are firstly linear isomerisation of 1-hexene followed by skeletal isomerisation and finally dimerisation and cracking (see figure). The model is tested by using a skeletal hexene isomer – 2,3-dimethyl-2-butene (DMB) – as reactant.



Ability of the sequential reaction model to predict the dimerisation of 1-hexene at 200 °C: Δ =1-hexene, \circ =linear hexene isomers, \square =skeletal hexene isomers and \diamond =overall hexene depletion

Nomenclature

A	1-hexene
B	linear hexenes
C	branched hexenes
C_i	concentration of component i (mol/l)
D	oligomerised and cracked products
DMB	2,3-dimethyl-2-butene
k_i	rate constant of reaction i (l/(g min))
m_{cat}	catalyst concentration (g/l)
SPA	solid phosphoric acid
t	time (min)

Article Outline

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1. Introduction

The oligomerisation of olefins allows the petrochemical industry flexibility in the production of gasoline and diesel from shorter chain olefins. This involves the use of a solid acid catalyst and in industry mainly ZSM-5 and solid phosphoric acid (SPA) are used [1] and [2]. Industrially, the oligomerisation of shorter chain olefins is more established in the production of petrol [3]. The oligomerisation of heavier olefins, such as 1-hexene, can however also be used for the production of diesel and lubricating oils [4]. In general, acid catalysed olefin oligomerisation may involve many different reaction steps, amongst which are: isomerisation (for C₄ and longer olefins), hydrogen exchange, dimerisation, trimerisation, etc., and cracking [5]. In previous studies on 1-hexene oligomerisation the reaction selectivity towards the formation of dimers, trimers, heavier products and cracked products was investigated as a function of solvent type [6] or catalyst type [7], [8] and [9]. Here, no distinction was made between the different hexene isomers since the entire isomer community was grouped together when selectivity was calculated. However, Quan et al. [10] showed that 1-hexene is readily isomerised by ZSM-5 and a wide spread of different hexene isomers are formed. This is also observed by authors who used SPA as catalyst [11], [12] and [13]. Since it is known that the reactivity, as well as the selectivity towards dimerisation, of the different isomers increase, with the degree of substitution of the carbocation [14], [15] and [16], the quality of the gasoline product produced can vary according to the distribution of the different isomers [17].

None of the previous studies on 1-hexene oligomerisation considered the rate of the reaction and more specifically the rate of formation and depletion of the different hexene isomers as part of the oligomerisation process. In this study the rate of 1-hexene dimerisation is studied over an SPA catalyst. Due to the importance of the isomer spread in the reaction mixture, the rate of formation and depletion of linear and skeletal hexene isomers and its subsequent effect on the overall rate of the reaction is considered. Possible reaction pathways are identified and the rates of the different reaction steps are quantified using simple first order rate expressions. This information on the relative reaction rates and pathways will give valuable information on how the isomer spread in

the reaction mixture will influence the overall reaction rate. The validity of the proposed pathways and kinetics is tested by direct dimerisation of a skeletal hexene isomer (2,3-dimethyl-2-butene). The reactions are studied at 150 °C, 200 °C and 250 °C in a batch reactor at 6 MPa.

2. Experimental

2.1. Materials

An industrially manufactured solid phosphoric acid catalyst C84/3 (properties listed in Table 1) from Südchemie Sasolburg was used in all the experiments. The catalyst was ground to less than 150 µm since identical reaction rates with catalyst particles smaller than 150 µm and 300 µm, respectively showed that internal mass transfer limitations are safely eliminated in this size range. Due to the hydrophilic nature of the catalyst it was also dried at 200 °C for 24 h before each run.

Table 1.

SPA catalyst properties [18]

Free acid (%)	22.4
Ortho-/pyro-silicon phosphate (XRD counts)	1.3:1
Total intrusion volume (ml/g)	0.25
Average pore diameter (Å)	279
Total pore area (m ² /g)	36

Two different hexene isomers – 1-hexene (97%) and 2,3-dimethyl-2-butene (DMB) (98%) – were used as reactants in separate experiments. A solvent, in this case tetradecane (99%), was used to ensure that the reaction remained in the liquid phase. All the chemicals were supplied by Sigma–Aldrich.

2.2. Analysis

Samples were analysed with an Agilent Technologies 6890 gas chromatograph (GC) fitted with a flame ionisation detector (FID). Elutriation was established on a 50 m long Pona column with a 0.2 mm inner diameter and a 0.5 mm film thickness with N₂ as carrier gas at a flow rate of 25 ml/min. A split ratio of 100:1 was used. The initial column temperature was 40 °C, where it was held for 5 min, after which the temperature was ramped to 300 °C at 8 °C/min where it was finally held constant for 5 min. Retention times of various hexene isomers were determined by injection of analytical grade standards from Sigma–Aldrich: *cis* and *trans* 2-hexene (85%), 3,3-dimethyl-1-butene (95%), 2-methyl-2-pentene (98%), 2,3-dimethyl-1-butene (97%), 2,3-dimethyl-2-butene (98%) and 2-ethyl-1-butene (95%). The rest of the hexene isomers were identified from the retention indexes given by Dietz [19]. Cracking of the dimerised product occurred

and a wide range of products (C_4 – C_{12}) were detected. For simplification the dimerisation and subsequent cracking was quantified as the depletion of the total hexene isomer fraction. No trimerisation or higher oligomer products were formed at any of the temperatures investigated and all the components were elutriated before the tetradecane solvent. Overlapping of formed oligomer product with the tetradecane solvent was excluded by the fact that the tetradecane weight fraction remained constant (maximum difference of 3% from start to end) throughout all the experimental runs. The lack of formation of trimer products for the dimerisation of 1-hexene was also noted by Nel and de Klerk [13] at similar reaction conditions.

2.3. Equipment and method

All the experiments were conducted in a 200 ml stainless steel batch reactor setup illustrated in Fig. 1.

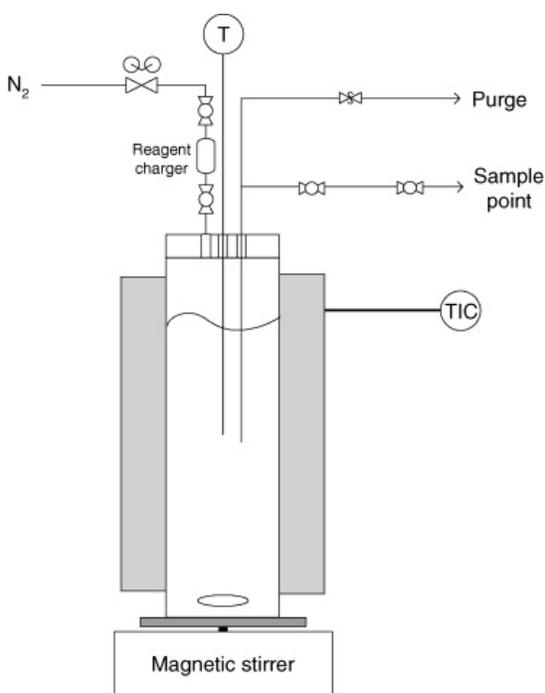


Fig. 1. Experimental setup.

The reactor pressure was controlled with a pressure regulator using a N_2 blanket. Approximately 5 g of the milled catalyst was loaded in the reactor vessel together with 75 g of solvent. This solvent/catalyst mixture was then heated to the desired reaction temperature at a pressure of 4 MPa. Once the temperature was reached, 35 g of the chosen hexene isomer were charged to the reactor from the charging vessel by increasing the pressure to 6 MPa—where it was controlled for the remainder of the reaction to ensure that the reaction mixture remained in the liquid phase at all the temperatures investigated. This was taken as the start of the reaction and a sample was taken at this

point to determine the exact initial mixture composition. Each sample was first cooled in a pressurised sampling train to prevent any atmospheric flashing. Although a slight drop in temperature (less than 5% of the setpoint temperature in °C), was observed after addition of the hexene reactant, the temperature was re-established before the next sample was taken where it was controlled within 1 °C of the desired setpoint using a heating jacket fitted with a temperature controller. The reaction mixture was agitated with a Heidolph 3001 MK magnetic stirrer at a rate of 1000 rpm after establishing that this would be sufficient to eliminate any external mass transfer effects (See Fig. 2). This procedure was repeated with both 1-hexene and 2,3-dimethyl-2-butene, respectively as reactant at 150 °C, 200 °C and 250 °C.

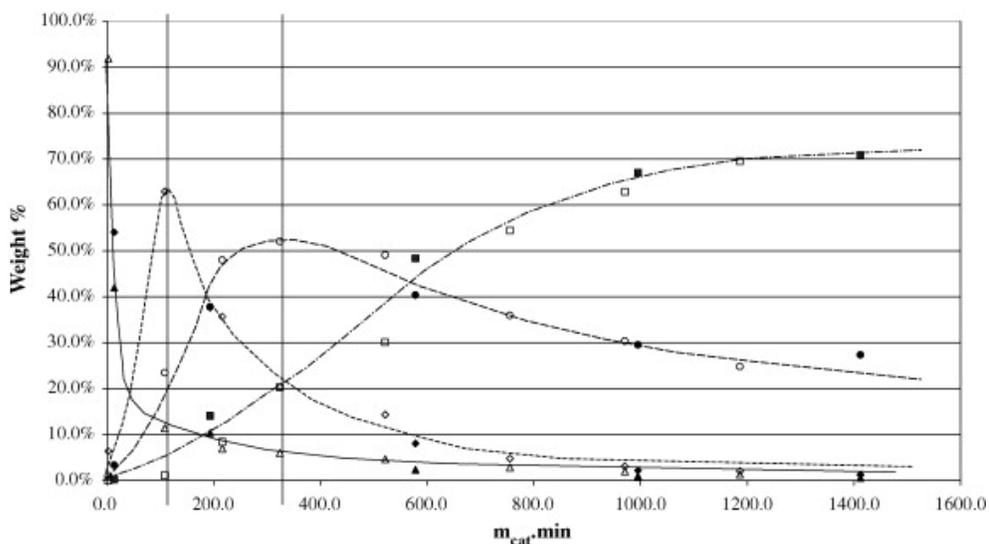


Fig. 2. 1-Hexene reaction progression at 250 °C versus weight time (m_{cat} min). Weight fraction of: (\triangle) 1-hexene (A), (\circ) linear hexene isomers (B), (\circ) skeletal hexene isomers (C) and (\square) overall hexene depletion (D). The stirrer speed is indicated by the open (500 rpm) and solid (1000 rpm) points.

3. Results and discussion

The formation and depletion profiles of 1-hexene (A), other linear hexene isomers (B), skeletal hexene isomers (C) and dimer and cracked dimer products (D) shown in Fig. 2 were observed at all the reaction temperatures investigated when 1-hexene was used as starting material. The solid points on the figure are from a run at 250 °C agitated at 1000 rpm and the open points at the same temperature but at 500 rpm. Similar levels of repeatability were achieved at other temperatures.

Based on these profiles the reaction pathway given in Fig. 3 is suggested for the dimerisation of 1-hexene (A), where the components are shown with their assigned symbols.

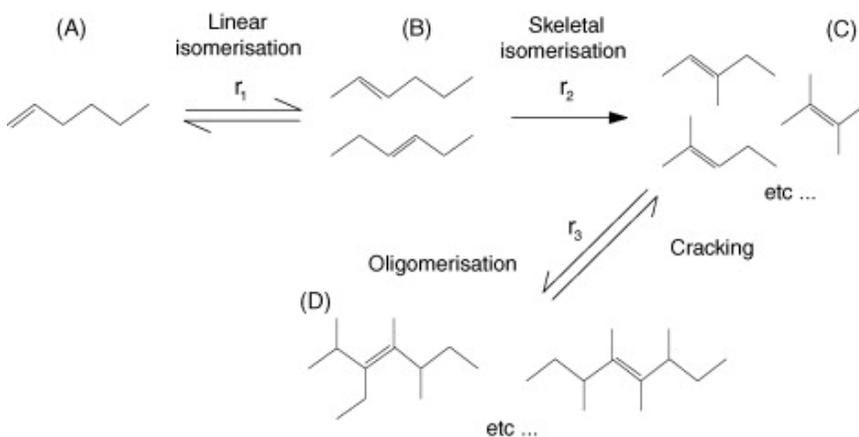


Fig. 3. A sequential reaction pathway is suggested for the dimerisation of 1-hexene.

The sequential nature of the reaction pathway is motivated by the S-shaped formation curves especially observed for C and D. Furthermore, the maximum seen in the profiles for B and C (indicated by the two vertical lines on Fig. 2) correspond to the inflection points in the profiles for components C and D, respectively. The product profiles suggest an equilibrium limitation on the formation of D – described here as the cracking of dimer product (D) to skeletal hexene isomers (C) – motivated by the plateau reached by D towards the end of the reaction time. The slow rate of depletion of A towards the middle of the run in Fig. 2 (compared to the rate at the beginning of the reaction) hints that equilibrium also exists between A and B and subsequently that A can only be completely depleted when all of B is converted. Finally, the rate data confirms the observation that skeletal olefin isomers are much more reactive towards dimerisation than their linear counterparts. For example, during the separation of isobutene and *n*-butenes by oligomerisation of the *iso*-butene, Scharfe [14], noticed that the conversion of *iso*-butene was almost complete while only limited co-dimerisation of the *iso*-butene and *n*-butenes occurred. Similarly Honkela and Krause [15] saw little dimerisation of 1-butene and 2-butene, even with the addition of *iso*-butene only some co-dimerisation occurred. de Klerk [16] saw a dramatic increase in the oligomerisation of 2,4,4-trimethylpentene compared to 1-octene when using solid phosphoric acid as catalyst. It is now postulated that for 1-hexene dimerisation over SPA this difference in reactivity is so significant that the direct dimerisation of B towards D can be neglected and that the proposed pathway represents the only reactions that needs to be considered for the development of a practical kinetic model. When all these observations are taken into consideration the reaction sequence can be modeled as a series of four elementary reactions described by the rate expressions given in Eqs. (1), (2), (3) and (4).

(1)

$$\frac{dC_A}{dt} = m_{cat} \left(-k_1 C_A + \frac{k_1}{K_{c1}} C_B \right)$$

$$(2) \quad \frac{dC_B}{dt} = m_{cat} \left(k_1 C_A - \frac{k_1}{K_{c1}} C_B - k_2 C_B \right)$$

$$(3) \quad \frac{dC_C}{dt} = m_{cat} \left(k_2 C_B - k_3 C_C - \frac{k_3}{K_{c3}} C_D \right)$$

$$(4) \quad \frac{dC_D}{dt} = m_{cat} \left(k_3 C_C - \frac{k_3}{K_{c3}} C_D \right)$$

With m_{cat} in (g/l), C_i is the product concentration (mol/l) corresponding to symbols assigned in Fig. 3, k_i and K_{ci} the rate constants and equilibrium constants for the corresponding reaction number (l/(g min)). An Arrhenius temperature dependence was assumed for all the rate constants. The values of the pre-exponential constants, activation energies and heats of formation of the reversible reactions (difference in the activation energies of the forward and reverse reactions) could then be solved by minimizing the square of the errors between predicted and experimental concentration values for all the components at the three temperatures investigated and are given in Table 2. The ability of the model to predict the experimental data is shown in Fig. 4a–c.

Table 2.

Equilibrium and rate constants for the reaction scheme proposed in Fig. 3

Rate or equilibrium constant	Pre-exponential constant	Activation energy (kJ/mol)	Heat of reaction (kJ/mol)
k_1	63,422 (g/(l min))	64.1	–
k_2	805.7 (g/(l min))	58.9	–
k_3	2.1×10^{-3} (g/(l min))	6.5	
K_{c1}	5.0×10^{-7}	–	–65.9
K_{c3}	0.149	–	–14.9

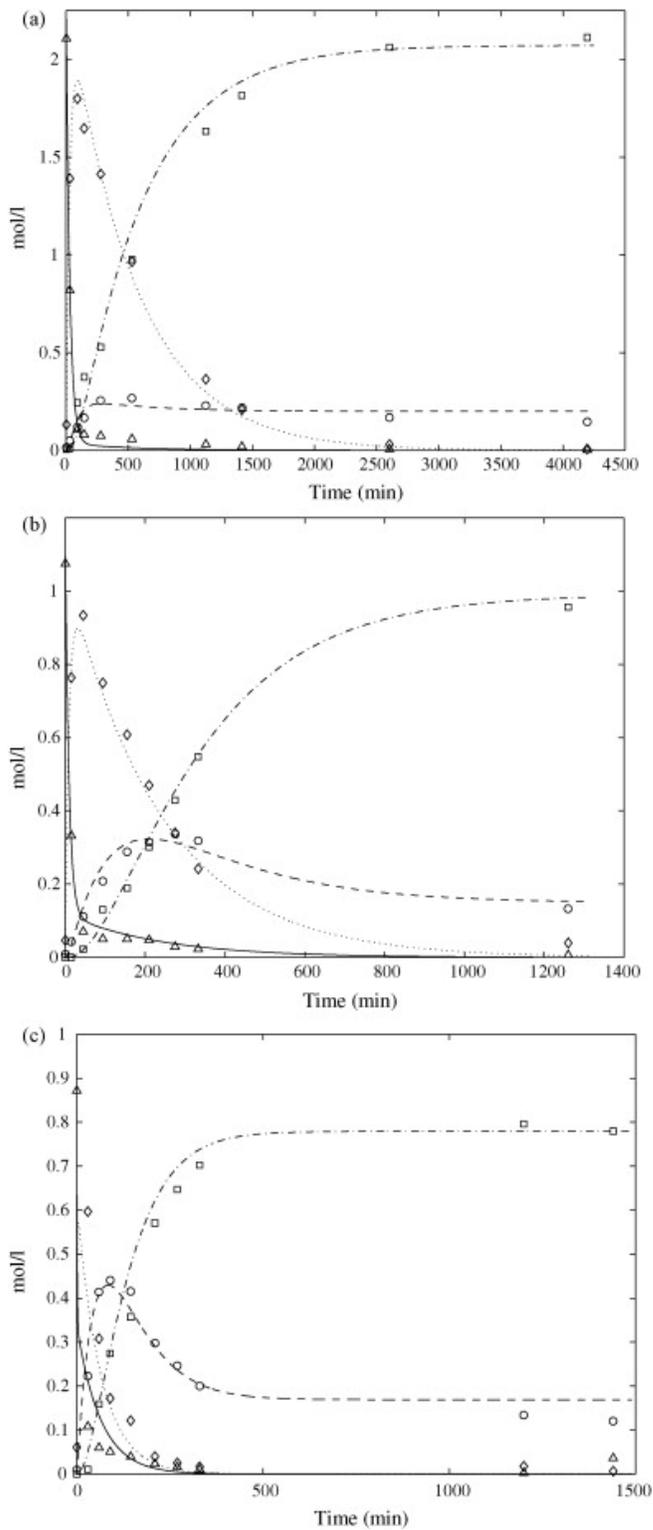


Fig. 4. Ability of the sequential reaction model to predict the concentration of: (△) 1-hexene (A), (○) linear hexene isomers (B), (◇) skeletal hexene isomers (C) and (□) overall hexene depletion (D).

The calculated heats of reaction indicate that both the equilibrium reactions – r_1 and r_3 – are slightly exothermic. The conversion of A to B (r_1) is significantly faster than all the other steps in the reaction sequence at all the temperatures—as emphasised in the Arrhenius plots of the rate constants given in Fig. 5. However, the rate constants for r_2 and r_3 are in a similar range. Subsequently the fact that the formation of C from B (k_2), is much more temperature dependant than the conversion of C to D (k_3) is significant. The ratio of these two rates is therefore a strong function of temperature.

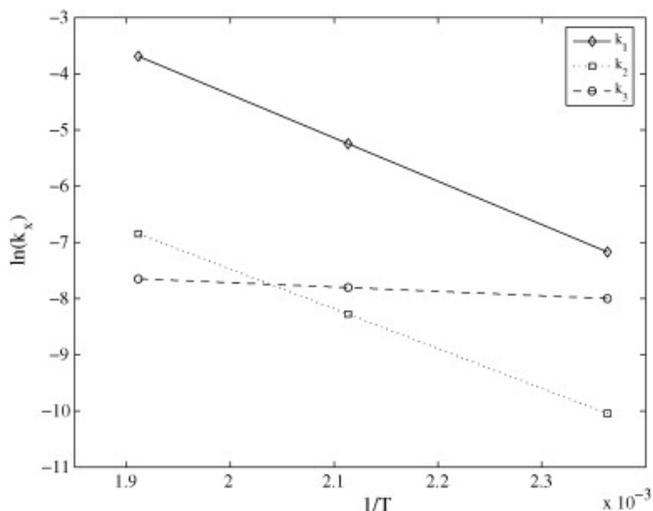


Fig. 5. Arrhenius relationship for the three reaction constants in the sequential reaction pathway.

The applicability of the proposed reaction scheme and resultant kinetic model was evaluated by using a skeletal hexene isomer (DMB) – i.e. only C – in the initial reaction mixture. Since only r_3 from the previous reaction scheme should then be active, Eq. (4) with the values of k_3 and K_{c3} given in Table 2 was used to model the reaction. The resultant prediction is compared to the experimental data in Fig. 6(a–c). It should be noted that small amounts of linear hexenes were formed during the reaction (less than 0.1%, 1.5% and 5% of the total reactive mixture at 150 °C, 200 °C and 250°, respectively). However, the linear hexenes were rapidly converted to branched isomers and were subsequently lumped with C.

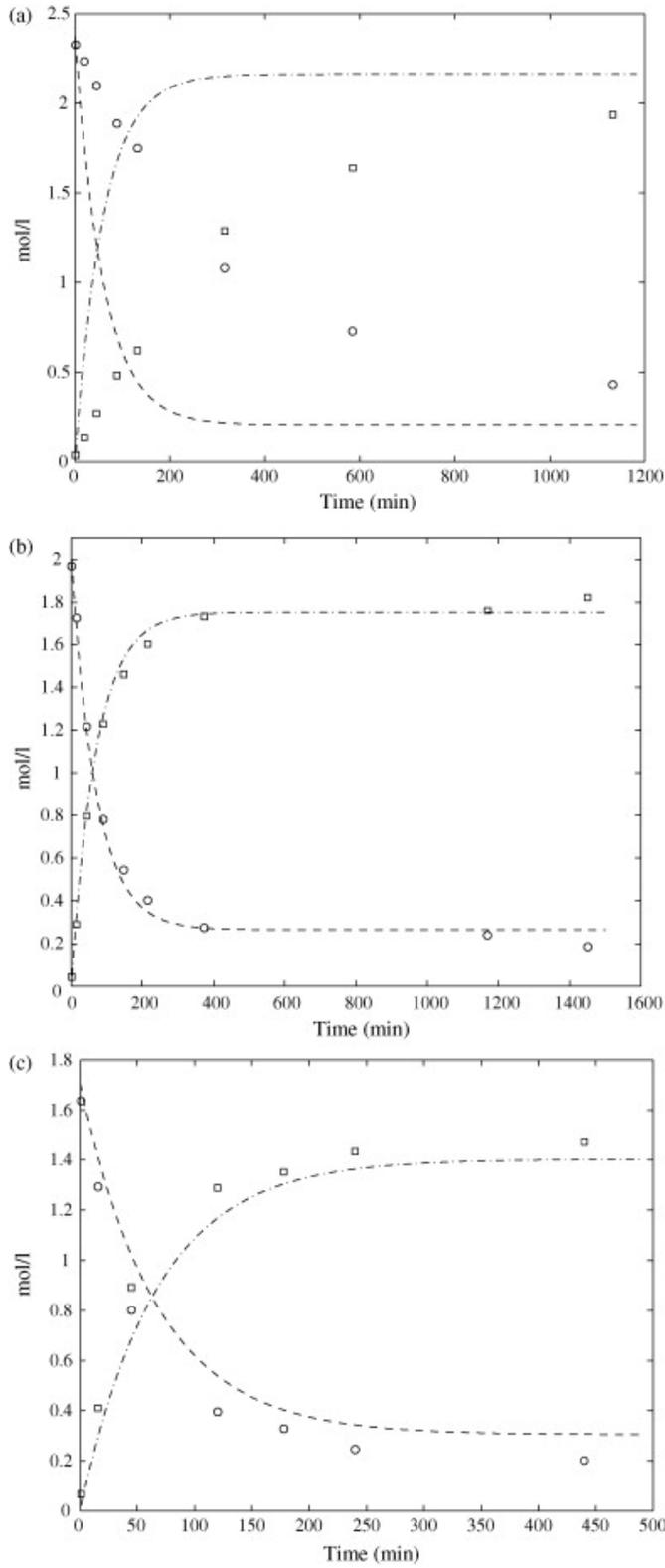


Fig. 6. Experimental versus predicted profiles of DMB (\circ) and hexene depletion (\square) at 150–250 °C.

While the model gives a very good representation of the experimental data at 200 °C and 250 °C, it fails to predict the reaction rate at 150 °C. If one assumes that all the skeletal isomers have similar reaction properties than that of DMB, the results suggest that a parallel pathway for the formation of D directly from B exists and that its relevance is directly linked to the temperature dependence of r_2 . At lower temperatures the significant temperature dependence of k_2 implies that B is converted to C at a much slower rate allowing the opportunity for B to be directly converted to D. Since the contribution of this pathway to the formation of D is lumped together with r_3 in the series model, the rate of formation of D is over predicted when no B is present in the reaction mixture. However, at 200 °C and 250 °C the contribution of the parallel conversion of B to D becomes negligible since B is rapidly converted to C as k_2 increases with temperature. It may therefore be possible to explain dominant reaction pathways by using the temperature dependence of competing reaction rates, but this idea requires further experimental support. An important observation is that the same equilibrium conversion of hexene is obtained for the 1-hexene and DMB runs at the different temperatures, despite the fact that the skeletal isomers formed when 1-hexene is used (mainly pentenes with a single methyl group) differs from DMB.

4. Conclusions

The rate data of the conversion of 1-hexene to dimers and cracked products suggest that the reaction pathway is of a sequential nature. Three reaction steps in series are postulated to model the reaction rate: linear isomerisation of 1-hexene followed by skeletal isomerisation and then dimerisation and cracking. The resultant elementary rate expressions give an adequate representation of the experimental data and shows that the linear isomerisation of 1-hexene is much faster than the other reaction steps in the sequence. Furthermore, the rate constant of the skeletal isomerisation step proved to be more temperature dependant than that of the other steps. By using only a skeletal hexene isomer (DMB) as reactant, it was shown that the proposed rate model fitted the data at 200 °C and 250 °C, but not at 150 °C. This suggests the relative importance of an additional reaction pathway (direct dimerisation of linear hexene isomers) at lower temperatures due to the high activation energy of the linear to skeletal hexene reaction rate. However, more work is required to prove the idea. The same equilibrium conversions of both 1-hexene and DMB were observed at all three temperatures investigated—suggesting that the equilibrium conversion is independent of the type of hexene isomer.

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