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Solid-State NMR Investigation of *n*-Heptane Cracking over Zeolite Beta

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n-Heptane cracking over zeolite H-Beta has been studied by solid-state NMR spectroscopy. It is shown that isomerisation and cracking are two related processes at the early stages of the reaction. Isomerisation is proposed to proceed faster than cracking via the intermediacy of protonated cyclopropane whereas cracking is suggested to progress through the classical β-scission route. Catalyst loading in the NMR experiments seems to be a very important factor for both initiation of the reaction and final product distribution. The initial source of *i*-butane, which is observed as primary product, is the isomer 2,2-dimethylpentane, which cracks to *i*-butane and propene. Propene, which has never been observed, is suggested to be involved in polymerisation reactions producing long hydrocarbon chains which can rearrange and finally crack to a number of C_5–C_7 isomers. At later stages, the reaction becomes very complex. More of the heptane isomers crack by β-scission to a number of C_4 and C_3 fractions. The carbenium ions desorb as paraffins by H-transfer while the olefinic fraction is involved in polymerisation reactions. At the final stages of the reaction, protolytic cracking starts contributing to this process, producing methane, ethane, and propane. Of great interest is the catalyst loading effect on this monomolecular reaction process which defines the final product distribution. © 1996 Academic Press, Inc.

INTRODUCTION

In the last forty years the highly important catalytic cracking process has stimulated an extraordinary amount of research leading to a number of mechanistic approaches which are based on either experimenal findings or theoretical studies. The enormous complexity of this reaction, coupled with the limitations of the techniques available to study this heterogeneous process, have always prevented scientists from grasping a complete understanding of this catalytic reaction. The classical bimolecular carbenium ion mechanism (1, 2) is a well-established theory which together with the more recent monomolecular carbonium ion mechanism (3) provides a satisfactory explanation for a large number of characteristic features of catalytic cracking. The factors favouring one or the other of these two mechanisms were thoroughly investigated and presented in a number of contributions (4–6). However, a great deal of scepticism concerning these two mechanistic approaches is shared by several researchers. Radical cation-like cracking on electron acceptor sites (EA) has long been suggested (7). Furthermore, of great interest is the recent work of S. Tiong Sie (8, 9) in which a considerable amount of experimental observations, which the classical bimolecular theory fails to explain, are listed. In those contributions a new mechanism is proposed which is characterised by the intermediacy of a nonclassical carbonium ion of cyclopropyl structure.

The use of mass spectrometry (MS) and ^{13}C-labelled (at certain positions) hydrocarbons as a technique to follow the fate of reactant hydrocarbon along the cracking process has already been demonstrated (10–14). Of great interest are the contributions of Daage and Fajula (13, 14) in which isomerisation and cracking of ^{13}C-labelled hexanes over H-mordenite are presented.

The potential of magic-angle spinning nuclear magnetic resonance (MAS NMR) for monitoring hydrocarbon conversions proceeding inside the catalyst pores using sealed samples has been widely demonstrated (15–25). Of particular relevance to our studies is recent work (25) employing MAS NMR and flow reactor/GC techniques. For instance, Nowak *et al.*, in their study of hexane cracking in ZSM-5, (25a) ascribed the differences in product distribution observed by NMR and flow reactor/GC experiments, especially the absence of olefins, to the difference in contact time in the two experimental setups. Moreover, it was clearly shown that at low temperatures (below 573 K) isomerisation reactions dominate while at higher temperatures cracking takes over.

In our studies the cracking of *n*-heptane over zeolite H-Beta was studied by means of MAS NMR. Although, zeolite H-Beta seems to be a potential commercial cracking and isomerisation catalyst, we did not focus on the catalytic properties of this material as such, but on the investigation of the cracking reaction mechanism. Nonetheless, where possible, the catalytic cracking features of this material are seriously considered.

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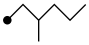
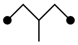
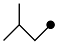
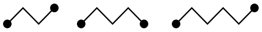
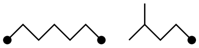
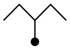
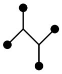
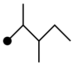
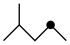
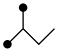
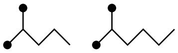
TABLE 1

Assignments of the Resonances Observed in this Work

Chemical shift (ppm)	Hydrocarbon
−11 to −10	CH_4
−10 to −8	CH_4 (ads)
3.5 to 6	CH_3CH_3
10.7	
11.5	
11.7	
13.5	
14.1	
15.1	
16	 (ads)
19	
19.4	
20	
20.8	
22	
22.4	
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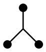
24.8	
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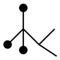
28	
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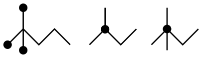
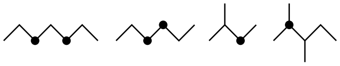
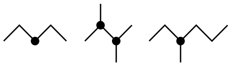
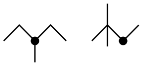
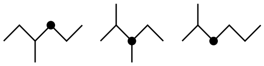
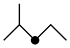
30	
32	
34	
36	
40	
42	

EXPERIMENTAL

Sample Preparation

Zeolite Beta in the acidic form was provided to us by Shell (KSLA). Chemical analysis of the calcined sample gives a Si/Al ratio of 17. Furthermore, this catalyst was fully characterised by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), ^{29}Si and ^{27}Al MAS NMR.

Catalysis-MAS NMR

n-Heptane (99% ^{13}C-enriched in one of the C_1 positions) was provided to us by Shell (KSLA). The catalyst (50 mg) was loaded into specially designed Pyrex capsules which were connected to a vacuum line. The catalyst was activated under vacuum at 673 K for 24 h and then loaded with a controlled quantity of the reactant. Our experiments were carried out with four different loadings, viz. 0.5, 1, 2, and 3.5 *n*-heptane moles per acid site. The sample capsules were sealed (15, 16) and heated at various reaction temperatures for a period of 3 min. All the ^{13}C MAS NMR spectra were recorded at room temperature on a Bruker MSL 400 spectrometer using a Chemagnetics APEX 400 pencil probe. These experiments were carried out by means of single-pulse direct excitation with high-power proton decoupling. Pulse delays of 5 s were found to be adequate to yield quantitatively reliable spectra. Chemical shifts are referenced either to external tetramethylsilane or to the silicon rubber sleeve used to hold the spinning samples. Background signals are denoted in our spectra and result from silicon rubber, 1.2 ppm, and spinning sideband (at spinning rate of ca. 5 kHz) of silicon rubber, 51 ppm.

RESULTS

All the ^{13}C MAS NMR spectra are presented in this section. As stated above, four major experiments were performed with four different loadings: 0.5, 1, 2, and 3.5 mol/acid site. Assignments (26) of all resonances in these spectra are listed in Table 1, where the dark dot denotes the carbon position to which chemical shift is referred.

Figure 1 shows the ^{13}C MAS NMR spectra for *n*-heptane cracking over zeolite beta at a range of temperatures where the loading of catalyst is 3.5 mol of *n*-heptane per acid site. Initially (293 K), four resonances are observed at 14.1, 23, 29.4, and 32 ppm, which are assigned to C_1, C_2, C_4, and C_3 carbons of *n*-heptane, respectively. The strong intensity of the C_1 signal results from the selective ^{13}C enrichment in this position. Reaction commences at ca. 423 K with the appearance of signals at 22.4 and 24.8 ppm. The resonance at 22.4 ppm is assigned to 2-methylhexane while the line at 24.8 ppm is characteristic of *i*-butane. After exposure of the system at 473 K, the *i*-butane resonance (24.8 ppm) increases noticeably while a new line appears at 30 ppm, which is assigned to 2,2-dimethylpentane. The C_5 signal of 2,2-dimethylpentane cannot be observed because it comes very close (ca. 15 ppm) to the C_1 signal of *n*-heptane and is relatively very weak. In addition, a number of weak resonances are observed at 11.5, 11.7, 16, and 19.4 ppm, which correspond to 3-methylpentane (11.5 ppm), 2-methylbutane (11.7 ppm), propane (16 ppm), and 2,3-dimethylbutane (19.4 ppm). Moreover, partial scrambling of the carbon atoms is evident in this spectrum by the presence of weak lines at 20.8 and 40 ppm, which are attributed to 2-methylpentane (C_4 position) and a number of heptane isomers (C_3 and C_4 positions), respectively. The next two spectra (523 and 573 K) exhibit mainly the same peak patterns as the previous one. Of great interest is the considerable increase of *i*-butane (24.8 ppm) and 2,2-dimethylpentane (30 ppm) lines. Moreover, due to the formation of 2,4-dimethylpentane, the resonance at 23 ppm is considerably enhanced (C_1 signal of 2,4-dimethylpentane overlaps with C_2 signal of *n*-heptane). More partially scrambled products are also observed at 23.8, 34, and 42 ppm. In the next spectrum corresponding to the temperature of 623 K, a number of important catalytic events can be seen. The lines of *i*-butane (24.8 ppm), 2-methylhexane (22.4 ppm), and propane (16 ppm) are enhanced markedly while the ^{13}C-enriched C_1 signal of *n*-heptane (14.1 ppm) is decreased dramatically. The formation of 2-methylpentane could also contribute to the enhancement of the line at 22.4 ppm. In addition, two shoulders appear at 13.5 and 25.1 ppm, which are assigned to C_1 and C_2 carbons of *n*-butane, respectively. The C_1 of *n*-pentane and *n*-hexane could also contribute to the line at 13.5 ppm. In the same spectrum, the relative increase of the lines at ca. 30, 32, 34, 36, 40, and 42 ppm is mainly due to the formation of more scrambled products. At the temperature of 673 K, *i*-butane (24.8 ppm), *n*-butane (13.5 ppm), and propane (16 ppm) signals continue to increase while the *n*-heptane C_1 line decreases constantly. The last two spectra indicate 100% conversion of *n*-heptane. The propane line (16 ppm) dominates in these spectra while the *n*-butane and *i*-butane lines are considerably decreased. In addition, weak signals of C_5 and C_6 isomers are still present while traces of methane and ethane give rise to weak lines at −11 and 3.5 to 6 ppm, respectively. The resonance at 15.1 ppm which appears in the last three spectra is assigned to propane (C_1) in the gas phase.

Figure 2 shows the ^{13}C MAS NMR spectra of *n*-heptane cracking over zeolite beta at a range of temperatures where the loading of catalyst is 1 mol of *n*-heptane per acid site. In accord with the previous experiments (Fig. 1), the reaction begins at 423 K. The relative intensity of the *i*-butane line (24.8 ppm) still parallels the one of 2,2-dimethylpentane (30 ppm) in the very early stages of the reaction. Furthermore, the 2-methylhexane line (22.4 ppm) seems to accompany the two resonances mentioned above in these early stages of the reaction. The spectra corresponding to higher temperatures are comparable to the ones of the previous experiments. Distinct differences are observed in the spectra of the final stages of the reaction. The methane and ethane signals are markedly stronger than the corresponding ones in the previous set of spectra. The *i*-butane and *n*-butane lines become relatively very weak while the resonances of C_5 and C_6 isomers are no longer observed.

Figure 3 shows the ^{13}C MAS NMR spectra of *n*-heptane cracking over zeolite beta at a range of temperatures where the loading of catalyst is 0.5 mol of *n*-heptane per acid site. As expected, the reaction commences at 423 K, with the formation of *i*-butane as the primary product. In the spectrum at 423 K, besides *i*-butane (24.8) and 2-methylhexane (22.4) a line at ca. 28 ppm appears, which is assigned to 2,2,3-trimethylbutane. In the expanded region of this spectrum we can also observe the presence of 2,2-dimethylpentane as a small shoulder on the C_4 signal of *n*-heptane. Due to both low loading and conversion the detection of weak resonances in this spectrum is not practically feasible. The spectra corresponding to higher temperatures exhibit the main features observed in the two previous sets of spectra. However, total conversion of *n*-heptane is reached at ca. 673 K and the main lines which have appeared in the corresponding spectrum are *n*-butane (13.5 and 25.1 ppm), propane (15.1 and 16 ppm), and *i*-butane (24.8 ppm). At higher temperatures (723–743 K), propane lines dominate in the spectra, while the lines of the butanes are dramatically decreased. Furthermore, methane and ethane lines appear in these spectra and their intensity is noticeably strong.

Summary of MAS NMR Results

In the above sections we have seen how the reaction proceeds inside the pores of the catalyst loaded with differ-

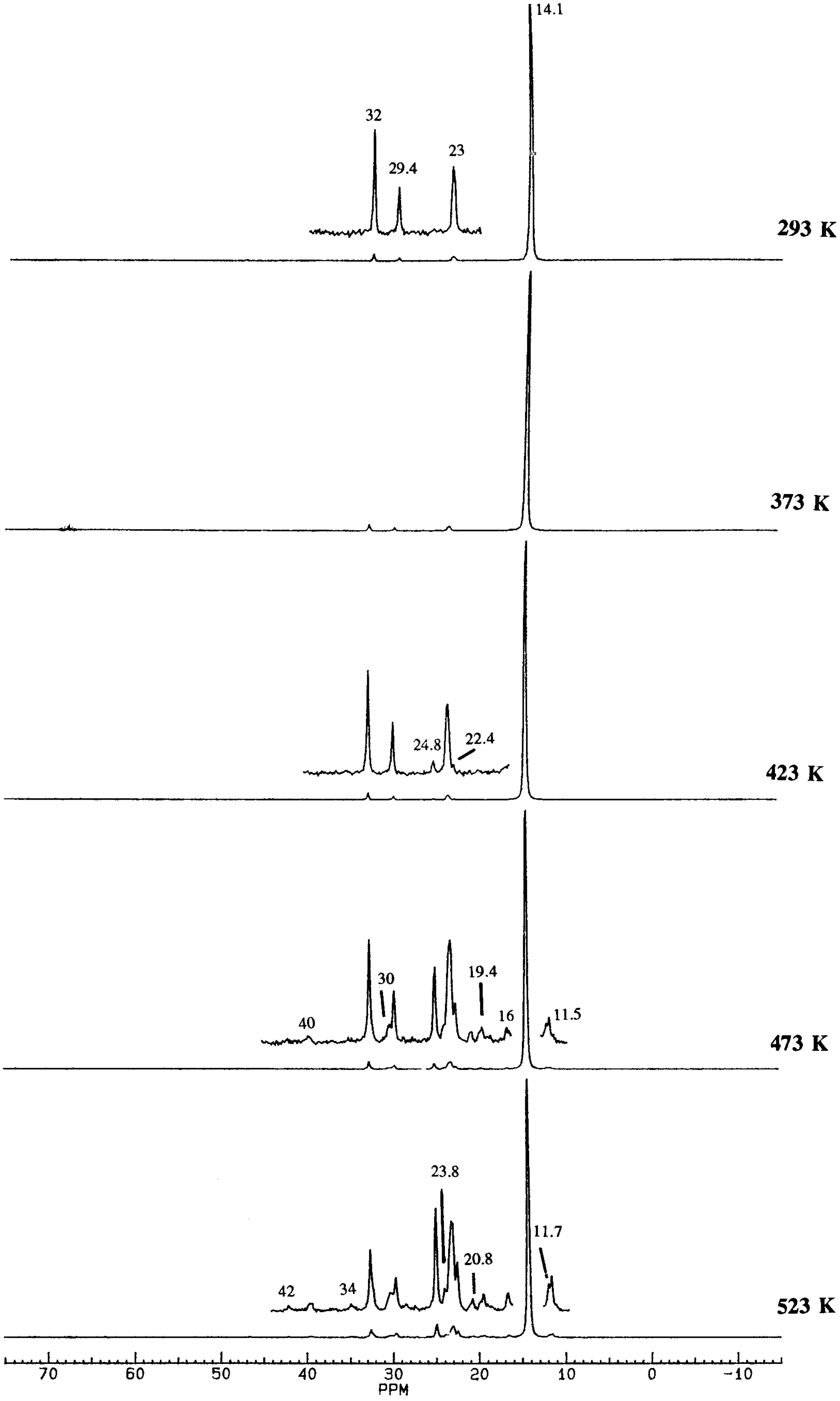


FIG. 1. ^{13}C MAS NMR spectra of *n*-heptane cracking over zeolite beta (3.5 m/a.s.).

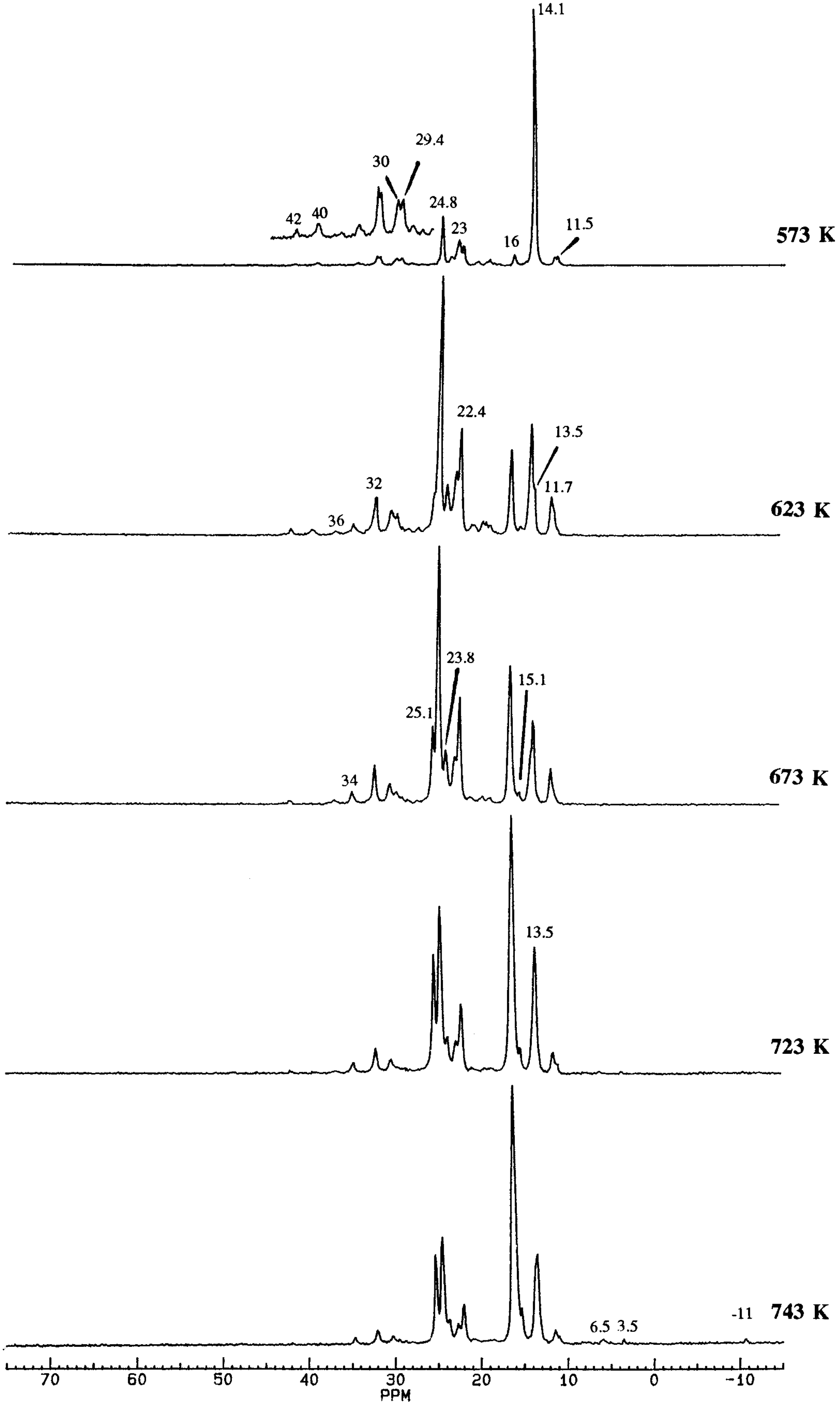


FIG. 1—*Continued*

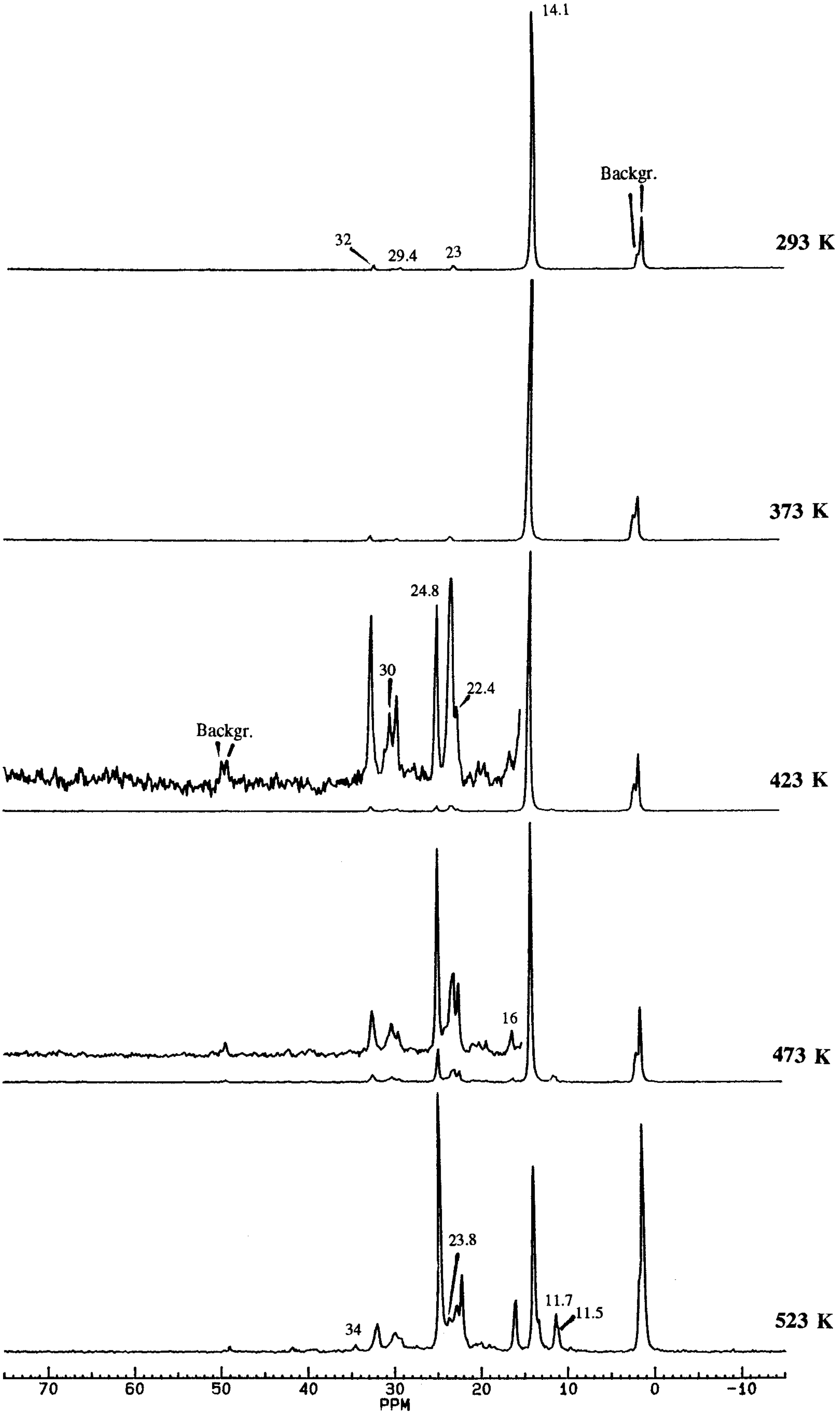


FIG. 2. ^{13}C MAS NMR specra of *n*-heptane cracking over zeolite beta (1 m/a.s.).

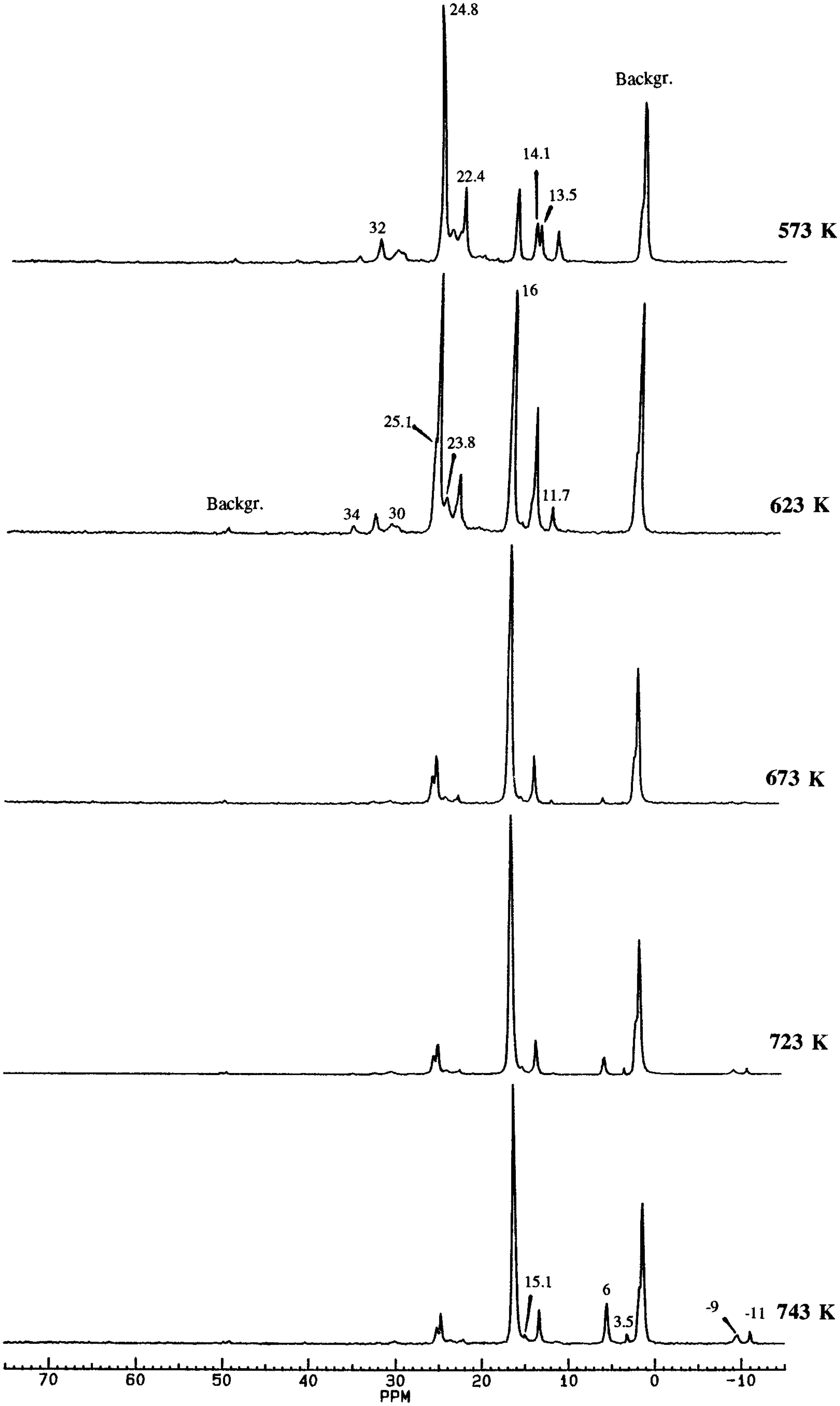


FIG. 2—*Continued*

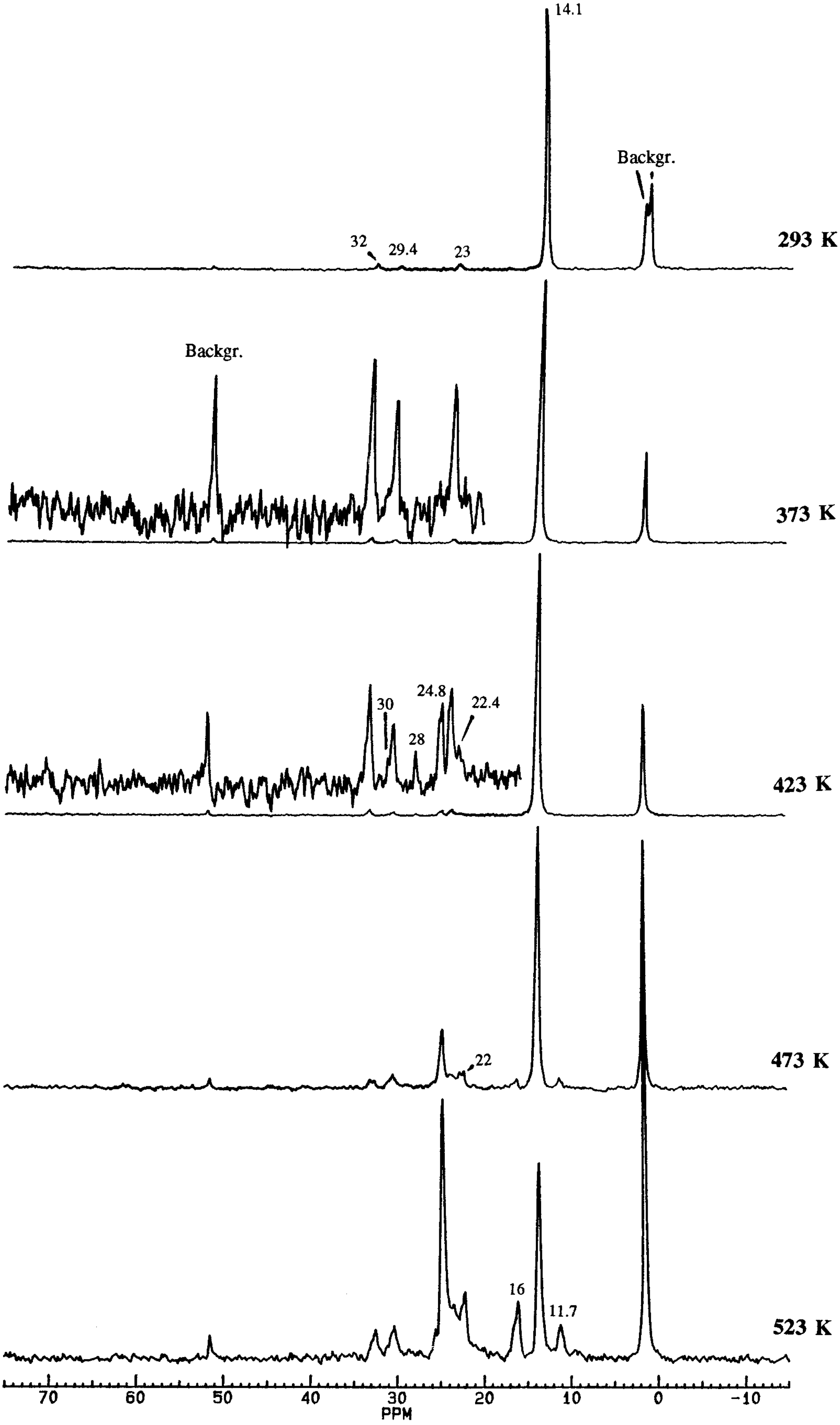


FIG. 3. ^{13}C MAS NMR spectra of *n*-heptane cracking over zeolite beta (0.5 m/a.s.).

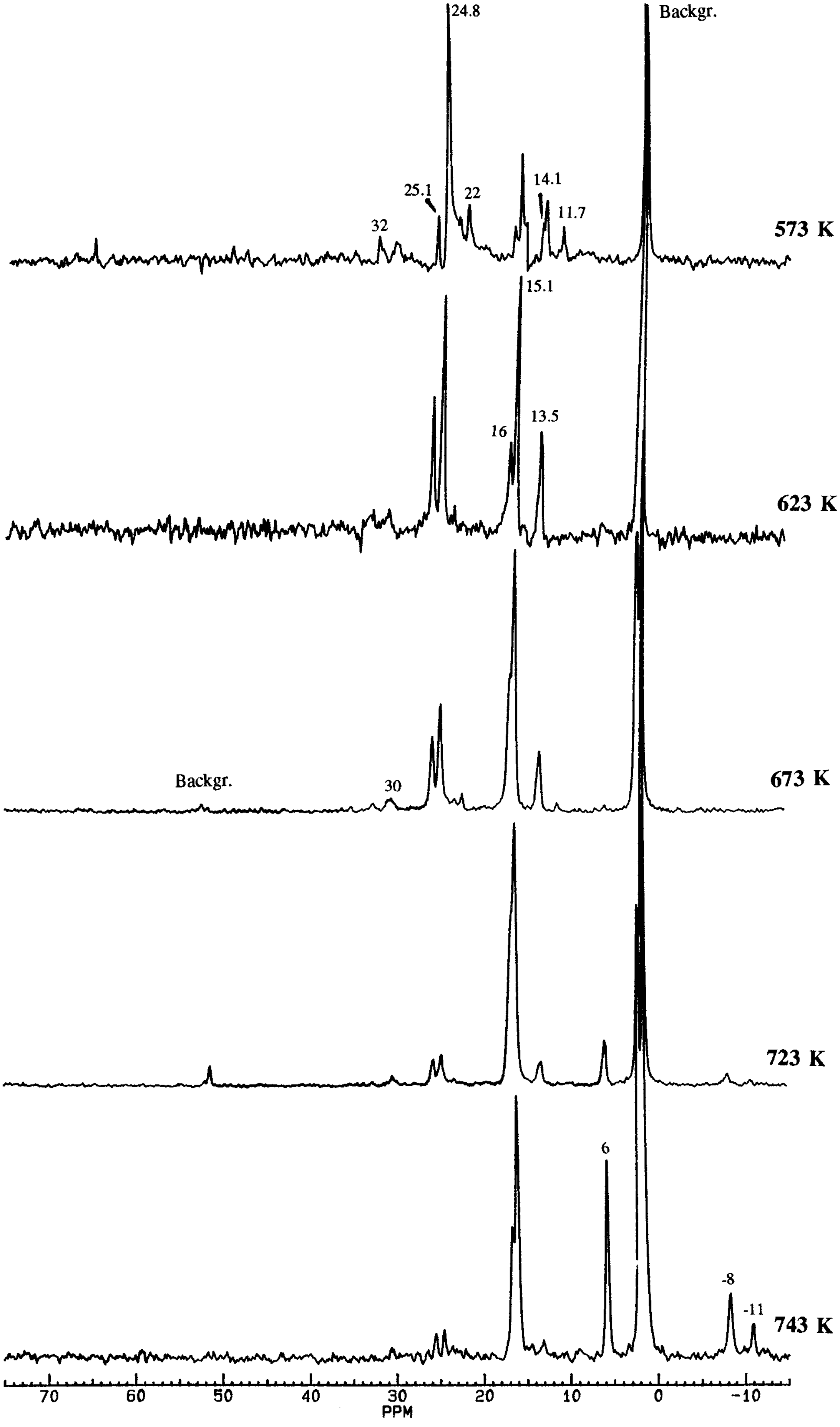


FIG. 3—*Continued*

ent amounts of reactant and heated at various temperatures. Overall, a similar catalytic behaviour was observed during these four experiments. However, a few differences, in particular at the very beginning and end of the reaction, are also noticed. The information deriving from both similarities and differences in these four experiments as well as the general progression of the reaction at different stages are very vital. These experimental findings can be briefly listed as:

1. The reaction commences at 423 K with the formation of *i*-butane as the primary cracking product.
2. Isomerisation of *n*-heptane seems to accompany the cracking process and the major isomers observed in the very early stages of the reaction (423–473 K) are 2,2-dimethylpentane and 2-methylhexane. The formation of the 2,2-dimethylpentane isomer seems to parallel the formation of *i*-butane (Fig. 6a).
3. Figures 4 and 6a illustrate that the relative amounts of *i*-butane and C_7 isomers (mainly 2,2-dimethylpentane) decrease with increasing catalyst loading at the very beginning of the reaction.
4. At higher temperatures (523–623 K), *i*-butane and propane lines dominate in the spectra while *n*-butane lines start appearing. In addition, resonances assigned to a number of C_5, C_6, and C_7 isomers become apparent. Scrambling of some products is also evident in this series of spectra.
5. At even higher temperatures (673–743 K) propane lines indeed dominate in the spectra while *i*-butane and *n*-butane lines tend to decrease dramatically (Fig. 5). Furthermore, methane and ethane lines are observed in the spectra corresponding to these high temperatures. Figures 6b and 6c illustrate the effect of catalyst loading on the selectivity for the final products. Low loadings favour the formation of methane, ethane, and propane while the final selectivity for *i*-butane is enhanced by increasing loading.

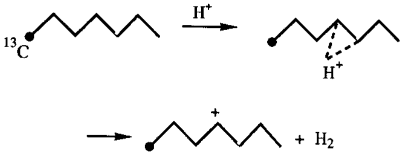
DISCUSSION

The First Stages of the Reaction

In the NMR experiments conversions are well controlled, achieving values lower than 1%. Consequently, the products observed at these conditions do indeed give us information concerning the onset of reaction. In these experiments, the reaction commences at 423 K with the formation of *i*-butane as the primary product. The spectra corresponding to this temperature (Fig. 4) also indicate various degrees of heptane isomerisation. The main heptane isomers observed in this early stage of the reaction are 2,2-dimethylpentane and 2-methylhexane and the former seems to parallel *i*-butane formation (Fig. 6a). In the fourth experiment (0.5 mol/acid side) extensive isomerisation of *n*-heptane also seems to occur, resulting in the formation 2,2,3-trimethylbutane. Interestingly, the amount of reactant in the pores of the catalyst (loading) seems to affect the extent of isomerisation, which in turn influences quantitatively the cracking primary products. At this very early stage of the reaction, it is clear (Figs. 4 and 6a) that with low loadings, isomerisation and hence cracking proceed very freely while with high loadings, in the overcrowded pores, the rates of both isomerisation and cracking processes are dramatically limited. This could result from either the insufficient number of active sites to catalyse isomerisation and thus cracking, or reactant molecules themselves sterically inhibit each other to isomerise and hence to crack to smaller molecules. This points to a crucial and fundamental aspect of cracking mechanism: cracking and isomerisation are two related processes. In addition, the formation of *i*-butane as primary product and its particular dependence on the extent of isomerisation suggests that this product derives from the cracking of isomerised reactant species. This implies that isomerisation proceeds faster than cracking at the very beginning of the reaction.

On this basis, the appearance of 2,2-dimethylpentane as a main heptane isomer in our spectra strongly suggests that this dibranched heptane isomer is the initial source of *i*-butane. Moreover, this is in accord with energetic aspects. Activation energies for cracking of heptane isomers (by β-scission) have been reported in the literature (27). The lowest activation energy (16.8 kcal/mol) corresponds to 2,2-dimethylpentane, the cracking of which leads to the formation of propene and a tertiary *i*-butyl cation. Alternatively, one could suggest that *i*-butane also results from cracking of 2-methylhexane, as this heptane isomer also appears in the spectra corresponding to the early stages of the reaction. Cracking of 2-methylhexane to *i*-butane would involve primary carbenium ions and thus seems very unlikely to occur at such low temperatures (423 K). Therefore, it is suggested that the initial source of *i*-butane is the isomer 2,2-dimethylpentane, which cracks to propene and a tertiary *i*-butyl cation. This cation desorbs into the gas phase by H-transfer as *i*-butane, and the primary products are expected to be propene and *i*-butane.

Bearing in mind that the *n*-heptane used in these series of MAS NMR experiments is selectively ^{13}C-enriched in one of the C_1 positions (denoted by a dark dot) the following reaction schemes can be drawn, expressing the points addressed above:



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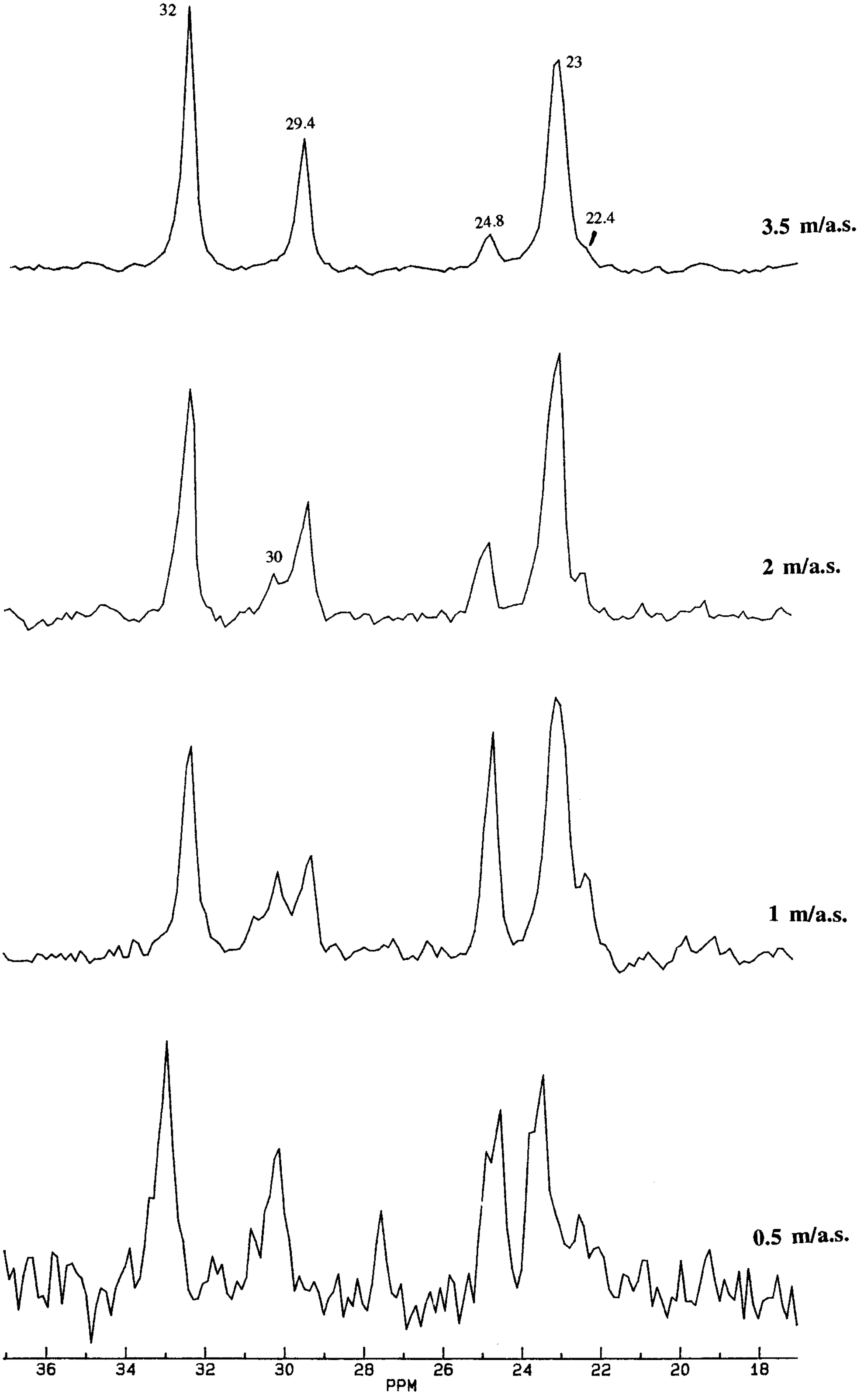


FIG. 4. ^{13}C MAS NMR spectra of *n*-heptane cracking over zeolite beta at 423 K.

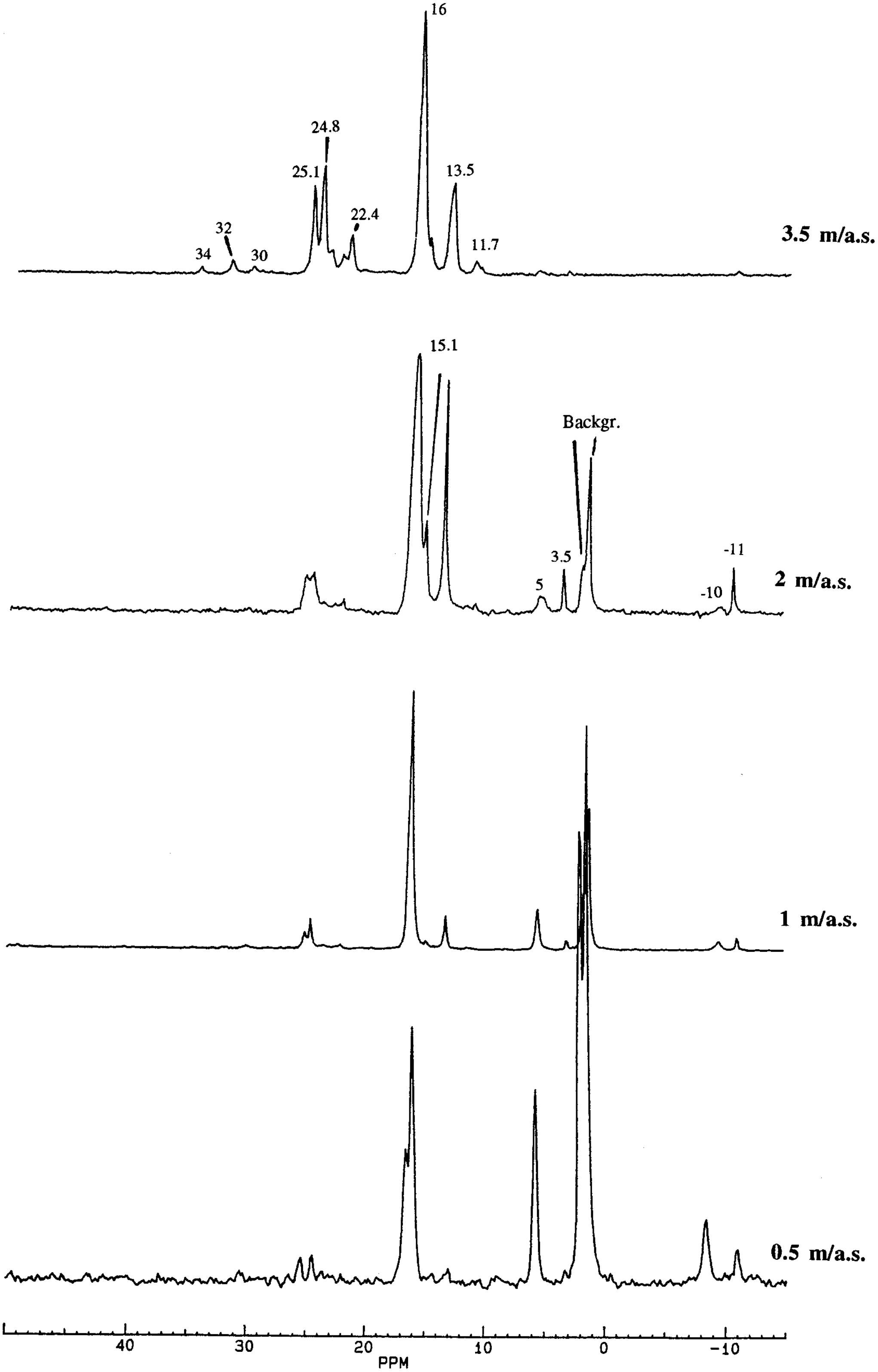
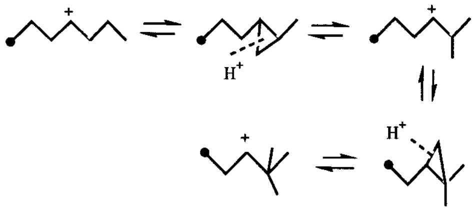


FIG. 5. ^{13}C MAS NMR spectra of *n*-heptane cracking over zeolite beta at 743 K.



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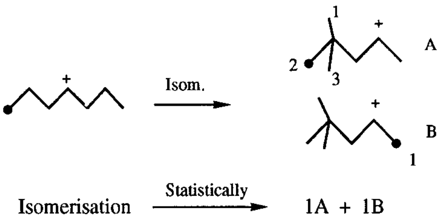

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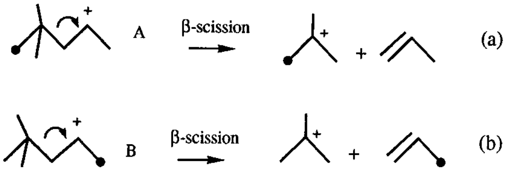


[4]

A number of interesting features shown in the reaction schemes above can be discussed. First of all, the observation concerning the relation of isomerisation and cracking processes suggests that the cracking reaction proceeds through the formation of carbenium ions. The formation of the very first carbenium ion in paraffin cracking is a rather controversial issue. A large number of proposed mechanisms have been reported (1, 2, 28) in the literature but without any conclusive proof. As shown in scheme [1], we suggest that a strong interaction between a Brønsted acid site and a reactant molecule leads to the formation of a secondary heptyl carbenium ion and molecular hydrogen. Isomerisation of this intermediate through simple hydride and alkyl shifts (carbenium ion-internal rearrangements) involves transformation of secondary to primary carbenium ions, a process which must be rejected on energetic grounds. However, an alternative route to isomerisation has already been proposed (8). This is characterised by the intermediacy of a nonclassical protonated cyclopropane, which can isomerise as shown in scheme [2] without the requirement of overcoming the energy barriers of primary carbenium ions. Such an isomerisation process can produce the two isotopic forms (A and B) of 2,2-dimethylpentane, as shown in scheme [3], in equal amounts. This is due to the distinctive fashion of rearranging the carbon chain by altering the internal carbon positions and leaving the terminal carbons intact. Isomerisation through the classical carbenium ions would involve terminal carbon rearrangements and thus produce the two isotopic forms in the ratio 3A : 1B. In that case, the ratio 3A : 1B is simply due to the fact that isomer A embodies three chemically equivalent and potentially labelled terminal carbon positions whereas isomer B contains only one. Having accepted the protonated cyclopropane (8) mechanism as the isomerisation route, one would expect to observe the C_1 and C_5 signals of 2,2-dimethylpentane in equal intensities. Unfortunately due to the very low conversion (weak signals) and the chemical shift of the C_5 resonance (15 ppm), it becomes impossible to observe this line and thus to support this proposal with some kind of spectroscopic evidence.

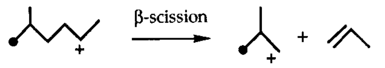
The protonated cyclopropane mechanism was not exclusively proposed for isomerisation but mainly for cracking. Cracking via this intermediacy indeed explains a number of experimental findings but it does not seem to be entirely in agreement with our results. The strongest argument against this mechanism is the formation of a large number of heptane isomers throughout our experiments and the remarkable dependence of cracking on isomerisation in the very early stages of the reaction. *n*-Heptane is the smallest molecule which, according to this mechanistic approach, can easily crack. Accordingly, once the intermediate complex, which is characterised by the cyclopropane structure, was formed, *n*-heptane would directly crack and not isomerise. This implies that no heptane isomers would appear in our spectra and hence there would be no dependence of cracking on isomerisation, something which cannot be supported by the experimental results of this work. Consequently, cracking via β-scission is the preferred route while isomerisation can easily proceed through the intermediacy of the cyclopropane structure, a process which is energetically favoured compared to classical carbenium ion rearrangements.

The next step of the reaction is cracking of heptane isomers (β-scission) as shown in scheme [4]. Assuming the intermediacy of cyclopropane as the isomerisation route, cracking of the 2,2-dimethylpentane isomer leads to the primary products shown in scheme (4). Reactions [4a] and [4b] must proceed in equal rates (A and B are formed in equal amounts) and thus the *t*-butyl cation and propene share 50% each of the original ^{13}C-label. The reaction is propagated by a bimolecular hydride transfer step between the *t*-butyl cation and *n*-heptane. This process leads to *i*-butane and propene as primary products. The fate of propene will be discussed later.

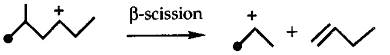
The other heptane isomer observed at the very beginning of this reaction process is 2-methylhexane. The line at 22.4 ppm which is assigned to 2-methylhexane could also be attributed to 2-methylpentane as the C_1 signal in these two paraffins comes at 22.4 ppm (Table 1). Hence, one could suggest that propene formed via scheme [4] is protonated to propyl cation and then oligomerises to 2-methylpentyl cation which in turn desorbs as 2-methylpentane by H-transfer. This would explain the absence of propene in the

NMR spectra. However, oligomerisation of propene to 2-methylpentane leads to an invalid H-balance and hence the line at 22.4 ppm is assigned to 2-methylhexane. The formation of 2-methylpentene as primary oligomer is in agreement with an H-balance but the absence of 2-methylpentene in the NMR spectra indicates that the chemistry involved at this reaction stage is far more complicated than simple oligomerisation reactions of the highly reactive olefins.

The formation of 2-methylhexane results from desorption of 2-methylhexyl cation by an H-transfer process. This cation is an intermediate step during isomerisation of *n*-heptane to 2,2-dimethylpentane, as shown in scheme [2]. Having accepted that isomerisation proceeds faster than cracking, it is proposed that a proportion of this isomer undergoes a cracking reaction (β-scission) whereas the rest of it either desorbs as 2-methylhexane (H-transfer) or isomerises further to 2,2-dimethylpentane (scheme [2]). Cracking of 2-methylhexyl cation to *i*-butyl cation, which in turn would desorb as *i*-butane (H-transfer), is not energetically feasible as primary carbenium ions would be involved (scheme [5]). Alternatively, 2-methylhexyl cation can crack to a secondary propyl ion and *n*-butene, a process which does not seem unreasonable (scheme [6]).



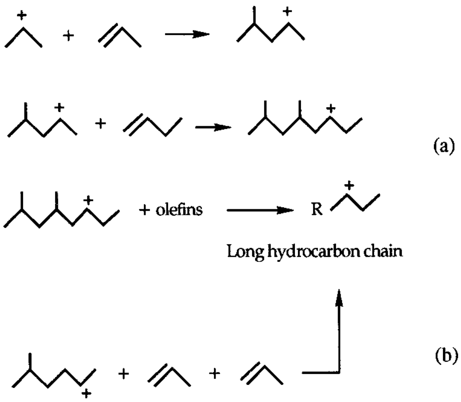
[5]



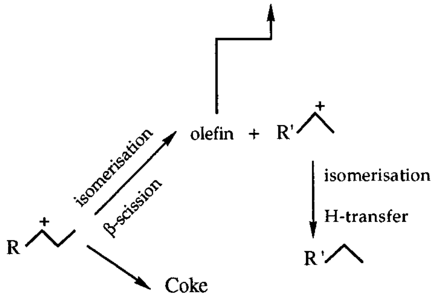
[6]

As stated above, cracking of 2,2-dimethylpentane results in the formation of *i*-butane and propene (scheme [4]). Furthermore, because of the distinct fashion of isomerising the *n*-heptane skeleton each of the two cracking products accommodates 50% of the original ^{13}C-label. This implies a ratio of 1 : 1 for *i*-butane and propene signals in the NMR spectra. Propene has never been observed in our spectra. Furthermore, propane and *n*-butene, which could be potentially formed by the cracking of 2-methylhexane (scheme [6]), have not been detected at these early stages of the reaction. This suggests that all these highly reactive species are involved in secondary reactions including polymerisation and isomerisation, forming large hydrocarbon chains (13, 14). Reaction scheme [7a] illustrates the formation of these long chains based on the highly reactive products of schemes [4] and [6], which are propene, *n*-butene, and secondary propyl carbenium ion. Alternatively, these long chains could also be formed by attachment of the 2-methylhexyl cation (or any heptyl cation formed during the isomerisation process in scheme [2]) to a number of propene molecules (scheme [7b]). In this case cracking of 2-methylhexane would not be needed in order to initiate the formation of these long chains. Once these long chains are formed they can either isomerise (protonated cyclopropane mechanism) and eventually crack (β-scission) to a variety of products, or initiate coke formation at later stages of the reaction (scheme [8]). The resulting carbenium ions either desorb as paraffins by H-transfer or undergo further rearrangements before desorbing. The olefinic fraction is involved in further polymerisation reactions.

Due to the low *n*-heptane conversion and the large variety of the cracking products (weak resonances), the products deriving from these long chains cannot be detected at these early stages of the reaction (423 K). However, at later stages (473–523 K) a number of C_5–C_6 paraffins are detected, some of which are partially scrambled. The formation of these products coupled with the complete absence of methane and ethane at this reaction stage, strongly suggests that these paraffins originate from these long hydrocarbon chains.



[7]



[8]

Rearrangements of the Carbenium Ions

As stated above, isomerisation is suggested to proceed via the intermediacy of protonated cyclopropane structure. The detection of isomerised and partially scrambled C_5–C_7 products coupled with the distinct positions of the scrambled carbons suggest a second fashion of rearranging these highly reactive intermediates. The factors affecting one or the other way of rearranging these intermediates are not to be examined in the present work.

Based on a number of hexane isomers observed at the early stages of the reaction and the positions in which

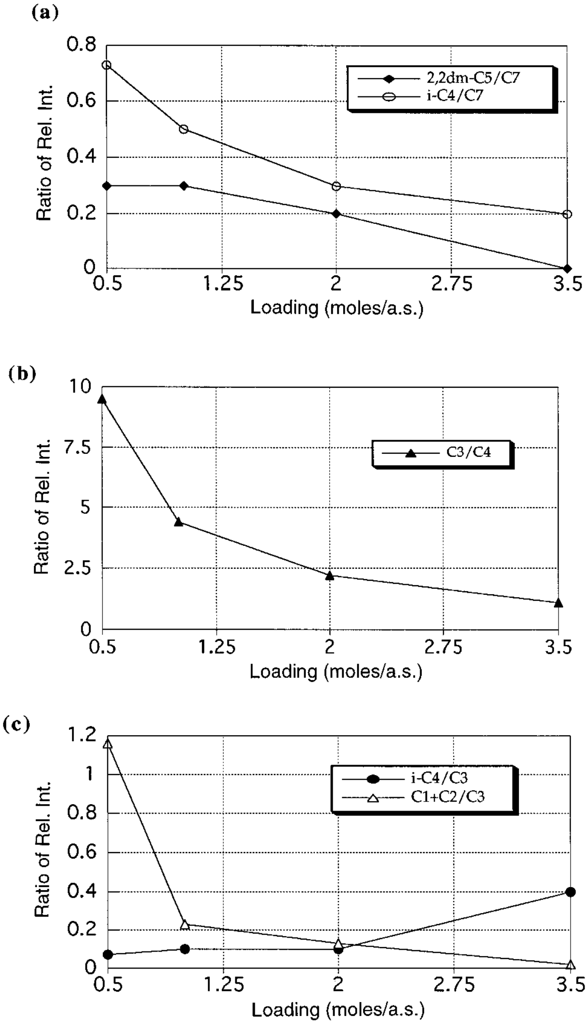
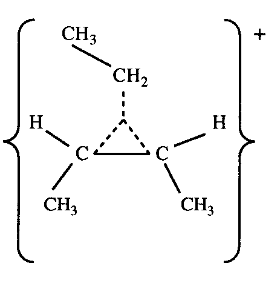
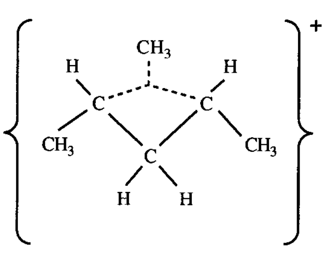


FIG. 6. Product selectivity of *n*-heptane cracking at: (a) 423 K, (b) and (c) 743 K.

the ^{13}C-label is accommodated, a number of interesting aspects can be discussed. The hexane isomers are taken as examples in this discussion whereas similar rearrangements are proposed to occur for all the C_5–C_7 products. The carbenium ions (hexyl cations) which derive from the long chain cracking (scheme [8]) can undergo a number of rearrangements before desorbing as paraffins. The intramolecular rearrangements of hexyl cations on H-mordenite have been investigated (14) by ^{13}C labelling and mass spectrometric analysis. According to this work, 2-methylpentane can be rearranged to a number of hexane isomers with 2-, 3-methylpentane, and 2,3-dimethylbutane skeleton. Branching rearrangement of 2-methylpentane to 2,3-dimethylbutane is suggested to proceed via the protonated cyclopropane mechanism, while further rearrangements can occur through 1,2-ethyl, 1,3-methyl, 1,2-methyl, and 1,2-isopropyl shifts. The transition states of these rearrangements were regarded as alkyl bridged cations where the migrating group is bound to two carbon atoms by a two-electron three-centre bond. Two of these transition states corresponding to 1,2-ethyl and 1,3-methyl shifts are shown below (using Olah's notation (29)).

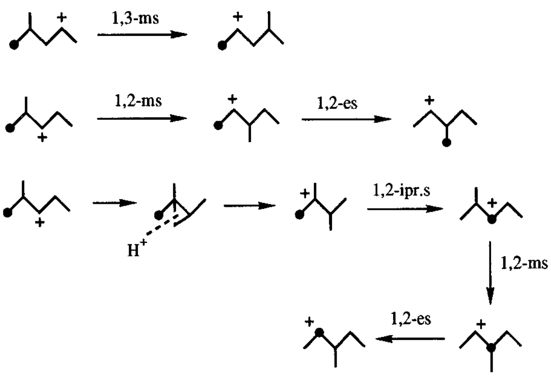


I



II

Assuming that cracking of a long hydrocarbon chain (scheme [8]) leads to the formation of a 2-methylpentyl cation and an olefin, reaction scheme [9] demonstrates a number of rearrangements which this cation can undergo (based on the rules mentioned above), producing a number of hexane isomers including partially scrambled isomers. All of these products have been observed in the NMR spectra. In scheme [9] ms indicates methyl shift, es indicates ethyl shift, and ipr.s indicates isopropyl shift.



[9]

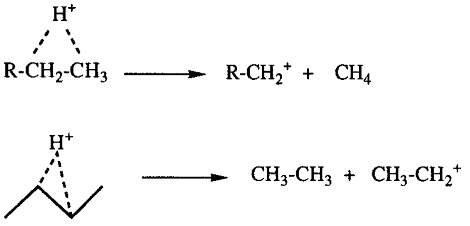
The Next Reaction Stages

As the reaction temperature is raised the reaction process becomes very complex. All of the heptane isomers formed (e.g., 2,4-dimethylpentane, 3-methylhexane) during this process can potentially crack to a number of C_3 and C_4 products. The carbenium ions, produced by β-scission, desorb as paraffins while the olefinic fraction is involved in polymerisation reactions forming large chains which after a number of rearrangements can eventually crack to a variety of products. The driving force for the constant increase of *i*-butane in these stages of the reaction seems to be the formation of tertiary carbenium ions. At higher temperatures, the formation of *n*-butane shows that the selectivity for these tertiary ions tend to decrease. Both, long chains and heptane isomers tend to crack to *n*-butane as the primary product. The relatively high degree of scrambling in the *n*-butane molecule must result from both the rearrangements in the large chains, from which this molecule originates, and intramolecular rearrangements through the protonated cyclopropane intermediacy. Any attempt of this molecule to isomerise through the cyclopropane intermediacy, as shown in scheme [10], would result in scrambling of its carbons (30) since primary carbenium ions would be involved otherwise. Furthermore, propane is produced in large amounts since both heptane isomers and hydrocarbon chains (resulting from oligomerisation/polymerisation processes) can eventually crack to an olefin and a secondary propyl carbenium ion which can desorb as propane.

[10]

Protolytic Cracking

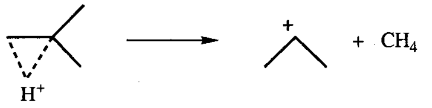
At the final stages of the reaction (Fig. 5), the formation of methane and ethane is a fingerprint of the high energy protolytic cracking process (3). *n*-Butane, *i*-butane, and the remaining C_5 and C_6 species can crack via a pentacoordinated carbonium ion (3) intermediate to form mainly methane and ethane as shown in Scheme [11]. Furthermore, protolytic cracking favours the formation of propane. It is clear that the initial catalyst loading can affect the rate of protolytic cracking which in turn directly defines the final product distribution. Low loadings favour protolytic cracking and hence the formation of methane ethane and propane (Figs. 6b and 6c). Conversely, with high loadings the contribution of protolytic cracking becomes less important. In this case, this must result from the limited number of strong acid sites, available at this final stage of the reaction, to form this high-energy pentacoordinated complex. Furthermore, the higher the contribution of protolytic cracking, the lower the final selectivity for *i*-butane. This implies that *i*-butane cracks much more easily than *n*-butane through this high energy intermediacy. This is indeed reasonable, since as shown in scheme [12], *i*-butane protolytic cracking leads to methane and a secondary propyl ion while protolytic cracking of *n*-butane unavoidably involves the formation of primary carbenium ions.



$$R\text{-}CH_2\text{-}CH_3 \longrightarrow R\text{-}CH_2^+ + CH_4$$

$$\longrightarrow CH_3\text{-}CH_3 + CH_3\text{-}CH_2^+$$

[11]



[12]

CONCLUSIONS

Isomerisation and cracking are two related processes at the early stages of the reaction. Isomerisation is proposed to proceed faster than cracking via the intermediacy of protonated cyclopropane while cracking is suggested to progress through the classical β-scission route. Once isomerised species are formed, further branching and nonbranching rearrangements can also occur through alkyl shifts. Catalyst loading in the NMR experiments is a very important factor for both initiation of the reaction and final product distribution. The initial source of *i*-butane, which is observed as the primary product, is the isomer 2,2-dimethylpentane which cracks to *i*-butane and propene. The other heptane isomer observed at the very early stages of the reaction is 2-methylhexane, which can potentially crack to a secondary propyl ion and *n*-butene. Propene, which derives from 2,2-dimethylpentane cracking, together with propyl ions and *n*-butene (2-methylhexane cracking) is suggested to be involved in polymerisation reactions producing long hydrocarbon chains which can rearrange and finally crack to a number of C_5–C_7 isomers. At later stages, the reaction becomes very complex. More of the heptane isomers crack by β-scission to a number of C_4 and C_3 fractions. The carbenium ions desorb as paraffins by H-transfer while the olefinic fraction is involved in the polymerisation reactions. At this stage, the formation of stable tertiary carbenium ions seems to be the driving force for *i*-butane production. However, at higher temperatures, as the reaction progresses the selectivity for *i*-butane formation decreases since the formation of secondary ions is also energetically feasible. This results in the formation of *n*-butane and a dramatic increase of propane.

At the final stages of the reaction, protolytic cracking starts contributing to this reaction process producing methane, ethane, and propane. Of great interest is the catalyst loading effect on this process. It is suggested that this high-energy process requires strong acid sites, the number and strength of which are dramatically reduced during reaction. Therefore, the higher the catalyst loading the lower the contribution of this process and hence the final yields of methane ethane and propane. It is also shown that the final selectivity for *i*-butane depends on the extent of the protolytic cracking reaction, i.e., the higher the protolytic cracking contribution the lower the selectivity for *i*-butane. Although *i*-butane is formed in considerably higher amounts than *n*-butane during this reaction process (particularly at the early stages), the final yields of these two products are comparable. In agreement with energetic considerations, *i*-butane cracks much more easily than *n*-butane via the protolytic cracking route.

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