A Molecular Orbital Approach to a Comprehensive Cracking Mechanism for Linear Long Chain Alkanes in Heterogeneous Acid Catalytic Conditions through Carbenium Ion β-Cleavage

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An extensive MINDO/3 theoretical study of the elementary steps of n-heptane cracking has been performed. A mechanism involving a carbenium ion is proposed and then a number of possibilities for further evolution of the different carbenium ions are considered. The energy surfaces for hydride transfer, β-cleavage processes either direct or concerted with 1,2-hydrogen shifts or concerted with a cyclic rearrangement, are explored. The energy barriers so obtained range over *ca.* 50 kcal mol^{-1} and are insensitive to product size. Consequently, the final product distribution cannot be explained in terms of the β-scission of linear n-heptane as the rate-limiting step. The β-scission energy barrier for some branched seven-carbon carbenium ions have been calculated to be *ca.* 30 kcal mol^{-1} an intermediate value between linear β-cracking and branching rearrangement transition energies. A mechanism is proposed that implies a fast achievement of equilibrium between different branched carbocations after carbenium ion generation by hydride transfer and then irreversible β-cracking.

The cracking of heavy hydrocarbons to yield fractions of lower molecular weight is a very important process in the petroleum industry. Heavy oils are converted into gasolines and gaseous hydrocarbons, either by heating only (thermal cracking) or, as is usual in industry, with the help of a catalyst (catalytic cracking).[1]

Thermal cracking is usually carried out over a temperature range of 823—923 K. The Rice–Kossiakof mechanism[2] is generally accepted[3,4] for thermal cracking. This mechanism involves a first step of homolytic C–C bond breaking to give two primary radicals which undergo further β-cleavage to yield ethylene and a new, smaller radical. This radical undergoes further β-cleavage until a methyl radical is formed. The chain mechanism continues through reactions of the methyl radical with neutral hydrocarbon molecules to yield methane and another radical that can undergo further scission and so on.

The whole process leads to the evolution of large amounts of ethylene and a small amounts of methane and α-olefins.

At present the most efficient solid acid catalysts available for hydrocarbon cracking are zeolites.[3] Most workers accept that the cracking reactions on acid surfaces proceed *via* carbenium ions.[1,3] The carbenium ion mechanism is also assumed for superacid homogeneous[5] and solid superacid heterogeneous[6] catalytic reactions.

As commonly accepted, the carbenium ion mechanism involves the β-cleavage[1,3,4,7] of the carbenium ions as they are formed. The β-cleavage of a linear carbenium yields another primary carbenium ion and α-olefin. In this way, only an electronic rearrangement is needed and thus the *principle of least motion* for elementary chemical reactions is achieved.[1,3,4]

The primary carbenium ion formed in this way could easily isomerize. It is noticeable that no ethylene can be obtained if only this mechanism is considered due to the relative instability of primary carbenium ions.

β-Cleavage is a very fast process if both starting and final ions are tertiary, but it is considerably slower when branching decreases, and it is especially difficult in cyclic compounds.[7] These facts are often explained in terms of the orbital orientation that allows an optimal overlap in the transition state.[7,8]

Otherwise, the catalytic cracking of long-chain paraffins gives high yields of fractions C_3—C_6 with a maximum at C_4.[3]

Instead of continuing to crack into smaller fragments, the carbenium ion can participate in a hydride transfer process from a paraffin to yield another paraffin and a new carbenium ion.[3,6,7] In this way, shorter alkanes and new large carbenium ions are produced and the overall reactions proceed *via* a chain mechanism.

Hydride transfer between tertiary carbons is an extremely fast process. The experimental barrier for the transfer of a hydride ion from secondary to tertiary carbon has been found to be <2 kcal mol^{-1} and the equilibrium constant corresponding to reaction (1) is near unity if R^{1+} and R^{2+} are

$$R^1\text{–}H + R^{2+} \rightleftarrows R^{1+} + R^2\text{–}H \qquad (1)$$

both tertiary or secondary and of the order of 10^{10} if R^{1+} is tertiary and R^{2+} secondary.[7]

The products pattern from catalytic cracking by acid zeolites at moderate temperatures have led some authors to suggest a parallel reaction that implies the disproportionation of the initial hydrocarbon molecule.[9–12] If Brönsted sites can be considered as the catalytic centres, that reaction is related to the protolytic addition described by Olah *et al.*[5] for superacid homogeneous catalysis of hydrocarbons. If disproportionation occurs after protolytic condensation, it may be that the mean life of the intermediate decreases as the temperature rises owing to the increase of vibrational energy, and simultaneously the probability of turning back to the original reactants increases, so that the disproportionation reaction is less important as the temperature rises.[9] On the other hand, if the disproportionation occurs through the interaction between the carbenium ion and the olefin to yield another carbenium ion which would follow a β-cleavage path, the temperature increase would disfavour this process because it implies an activation energy lower than that for cracking. Moreover, while alkylation is an exothermic process, the cracking is an endothermic one. So, from a thermodynamic point of view, a temperature increase will diminish the ratio of disproportionation to cracking.

Some previous results[12] suggested that disproportionation does not proceed through the carbenium–olefin interaction path. However, to obtain a definitive response, further studies that lie outside the scope of the present paper should be carried out.

We have performed an extensive theoretical study by using the semiempirical MINDO/3 approach.[13] We deal with the elementary steps of cracking in order to propose a detailed reaction path which explains the main features derived from the experimental evidence.

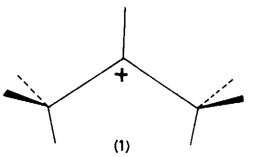
We have studied n-heptane (n-C_7) as a model for linear long-chain alkanes. Many data are available for this molecule.[11,12,14,15] It presents a carbon chain large enough to make its cracking yields and mechanisms comparable with that of the longer paraffins. Furthermore, we have considered as chemically equivalent the atoms on either side of the central carbon atom in order to obtain additional simplification.

Methodology

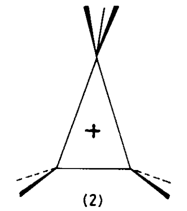
MINDO/3 is a useful tool in the study of some properties of organic ions, both classical and nonclassical in the gas phase, mainly regarding calculated values of energies, and also in the study of fragmentation reactions.[16] The extensive calculations of Dewar *et al.* seem to prove the applicability of the /3 version of MINDO to the study of chemical reactivity, since it is able to provide estimates of the energies of transition states that are as accurate as those associated with equilibrium states.[17]

Other features of MINDO/3 that have led us to make an extensive use of this method are as follows. (i) The use of a semiempirical approach allows us to perform inexpensive full geometry optimization, which is essential if one wants to perform a realistic study of processes involving carbocations and nonclassical species. Successful MINDO/3 studies on $C_6H_5^+$ [18] seem to confirm this fact. (ii) Since a single determinant Hartree–Fock approach does not take account in any way of the correlation effects, a limited *ab initio* study might likely lead to bad estimations of relative energies when cyclic or hydrogen-bridged molecules are involved in those cases where the difference between heats of formation are very small. However, MINDO/3 parametrization has been shown to incorporate the effects of the correlation energy [19] in some way.

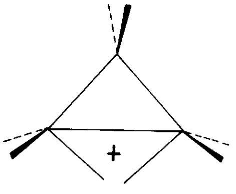
We have compared the relative energies of different arrangements of protonated propane obtained by different workers [20,21] using more accurate MO calculations, with our MINDO/3 results including full geometry optimization. It can be noted (see Table 1) that MINDO/3 gives very good results when compared with the best calculations including correlation energies, and much better than SCF only (even when an extended 6-31G basis set and full optimization are included[20]). MINDO/2 calculations on $C_3H_7^+$ molecule have been performed by Dewar *et al.*[22] by using the simplex method for geometry optimization. These authors do not report structure (**2**) as a stationary point whereas we have found that this structure is a saddle point at the MINDO/3 level.



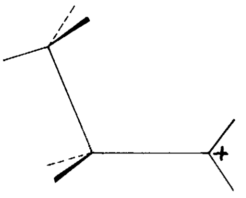
(1)



(2)



(3)



(4)

(iii) MINDO/3 calculations are useful in a great variety of cases in giving the correct order of the energies for alternative transition states and hence can be helpful in determining reaction mechanisms, at least to a first approach, and may serve as a starting point for more accurate *ab initio* calculations.[23] (iv) When applied to the study of hydride-transfer processes, MINDO/3 seems to be able to give suitable reaction maps to predict realistic mechanisms.[24]

We assume in this work that any chemical reaction occurs through the *minimum energy path* that connects reactants and products. This reaction path has been approximated by the method frequently referred as the reaction co-ordinate method,[25] so that, for each reaction under consideration, some geometrical parameters are adopted as independent variables and all the rest of the internal parameters are relaxed to a minimal energy for each point. In order to check that the maximum of the reaction path corresponds to a saddle point on the multidimensional energy hypersurface, *i.e.* which corresponds to a transition state, we have performed additional calculations over such a maximum in several significant reaction paths. First, by calculating the energy gradients we have proved that the maximum is stationary. Then we have calculated the force constant matrix for the geometry of the maximum and finally we have diagonalized that matrix. In all cases where we have realized this procedure we have found only one negative eigenvalue for the force constant matrix proving that we are concerned with true transition states. This procedure has been discussed elsewhere.[23]

All the geometrical optimizations were performed with the metric variable method described by Rinaldi.[26] All the calculations were performed with an updated version of the program system GEOMO.[27]

Results and Discussion

Hydride-transfer reactions occur simultaneously with the

Table 1. Total energies (kcal mol^{-1}) of the different arrangements of protonated propane obtained from MO calculations. All values are relative to structure (**1**) (2-propyl carbenium ion)

Structure	HF/4-31G[a]	HF/6-31G**[b]	MP2[b]	MP3[b]	MP4(SDQ)[b]	SCF1[c]	SCF2[c]	CEPA1[c]	CEPA2[c]	MINDO/3[d]
(**1**) 2-Propyl	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(**2**) Corner-protonated cyclopropane	17.3	13.4	4.7	7.2	8.2	16.4	16.8	7.2	7.5	12.1
(**3**) Edge-protonated cyclopropane	27.1	17.4	5.0	7.8	8.7	22.3	19.2	6.5	2.5	8.0
(**4**) 1-Propyl	19.4	18.8	19.9	19.8	19.7					20.0

[a] See ref. 20*b*. [b] See ref. 20*a*. [c] See ref. 21. [d] This work.

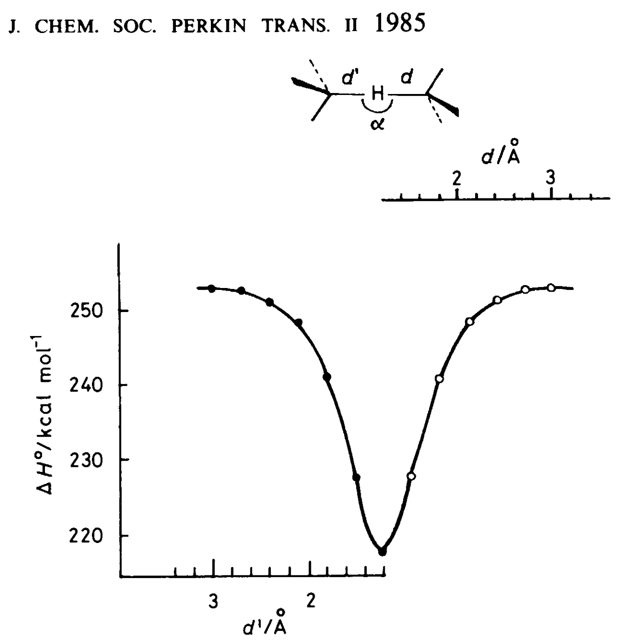


Figure 1. MINDO/3 energy profile for the hydride-transfer process $(CH_3 \cdots H \cdots CH_3)^+$

isomerization and cracking processes of saturated hydrocarbons in the presence of different acid catalysts. This transfer is a very fast process[3-6,14,28] and it has been suggested that paraffin cracking occurs *via* β-cleavage after previous formation of carbenium ions through a hydride-transfer reaction.[7]

The elementary model processes (2)—(4) were considered in order to determine the relative ease of hydride transfer in the set of elemental steps for overall cracking. MINDO/3 energetic profiles for these processes are shown in Figures 1—3. In all cases the distance *d* (see Figures 1—3) was adopted as the reaction-independent variable, and the angle α was fixed at 180°. The rest of the parameters were optimized.

$$CH_4 + CH_3^+ \longrightarrow CH_3^+ + CH_4 \quad (2)$$

$$CH_4 + (CH_3)_2CH^+ \longrightarrow CH_3'^+ + (CH_3)_2CH_2 \quad (3)$$

$$(CH_3)_2CH_2 + (CH_3)_2CH^+ \longrightarrow (CH_3)_2CH^+ + (CH_3)_2CH_2 \quad (4)$$

The results summarized in Figures 1—3 agree with the experimental data,[3,4,6,14,28] indicating the extreme ease of this elementary process, except for the production of primary carbenium ions where the hydride transfer becomes a very disfavoured step. The formation of primary carbenium ions would lead to the formation of ethylene through further β-cleavage.

The theoretical results are in good agreement with the experimental finding of lower yields of the C_2 fraction in cracking processes, showing the difficulty of forming primary carbenium ions.

Therefore the formation of primary carbenium ions from n-heptane will not be considered here, and we will suppose that the only significant heptyl ions concerning the main n-heptane cracking mechanism are 2-heptyl (1-methylhexylium ion), 3-heptyl (1-ethylpentylium ion) and 4-heptyl (1-propylbutylium ion).

β-Cleavage energy profiles have been obtained for these heptyl cations. First we have studied β-cracking in a direct way by lengthening the corresponding C–C bond. This process would only imply an electronic shift, which agrees with the principle of least motion for elementary chemical reaction steps.[1,3,4]

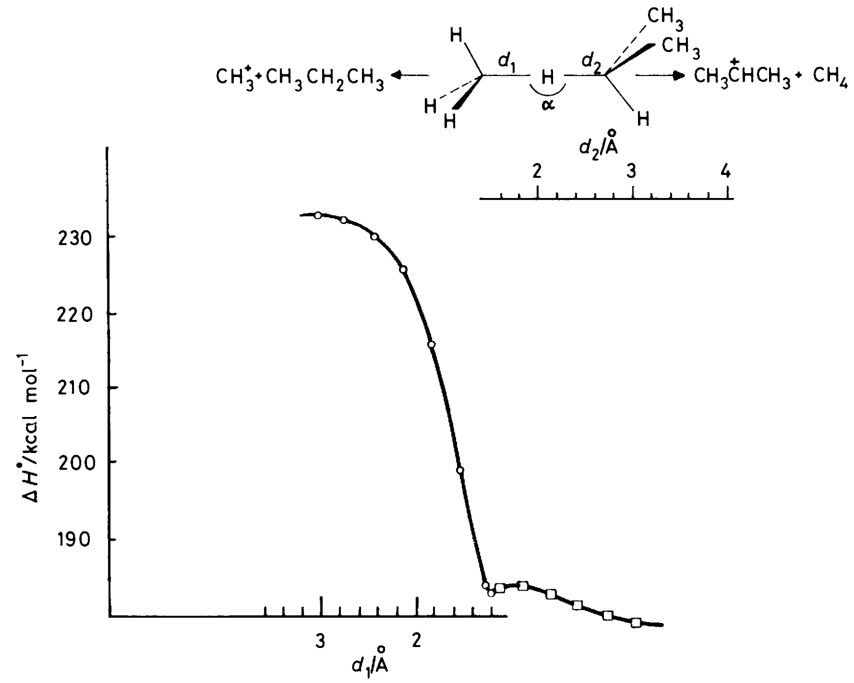


Figure 2. MINDO/3 energy profile corresponding to the hydride-transfer process $[CH_3 \cdots H \cdots CH(CH_3)_2]^+$

In Scheme 1 the β-cleavage processes that have been taken into account are shown. The parameter *d* represents the scanned distance. All the other internal parameters except the dihedral angle between the breaking bond and the vacant p_z AO over the carbene carbon atom (see Figure 4) were optimized. In this way, both the electronic density of the breaking bond and the vacant AO receiving electronic density are coplanar and a maximum overlap is allowed during the cleavage process as it was proposed by Brouwer and Hogeveen.[8]

The results of these calculations are summarized in Figure 5. The energy profiles show maxima that correspond to saddle points on multidimensional energy hypersurfaces according to

Scharfenberg.[29] As an additional proof we have diagonalized the force constant matrix for the maximum of profile B in Figure 5. Only a negative eigenvalue has been found, proving that the maximum is a transition state. Given the similarity of the chemical processes corresponding to all these profiles we have disregarded additional calculations over the other profiles. These profiles indicate the impossibility of β-cleavage to yield CH_3^+ (ΔE^+ *ca.* 92 kcal mol^{-1}), but the activation energies for the remaining cases are very similar and of the order of 50 kcal mol^{-1}. These results do not suffice to explain all the experimental evidence related to the cracking of linear heptane. For instance, the ratio ($C_3 + C_4/C_2 + C_5$) is much greater than unity[11] for the cracking of n-heptane over acid zeolite, and it is also noticeable that the differences between the experimental activation energies[12] for the processes $n\text{-}C_7 \rightarrow C_2 + C_5$ and $n\text{-}C_7 \rightarrow C_3 + C_4$ cannot be explained on the basis of the results shown in Figure 5.

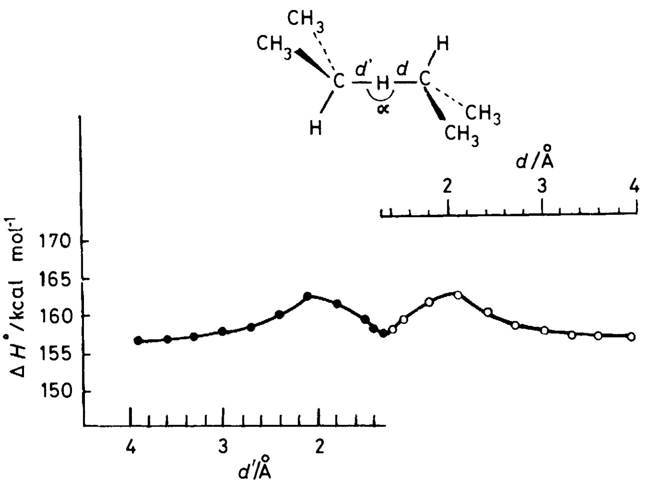


Figure 3. MINDO/3 energy profile corresponding to the hydride-transfer process $[(CH_3)_2CH \cdots H \cdots CH(CH_3)_2]^+$

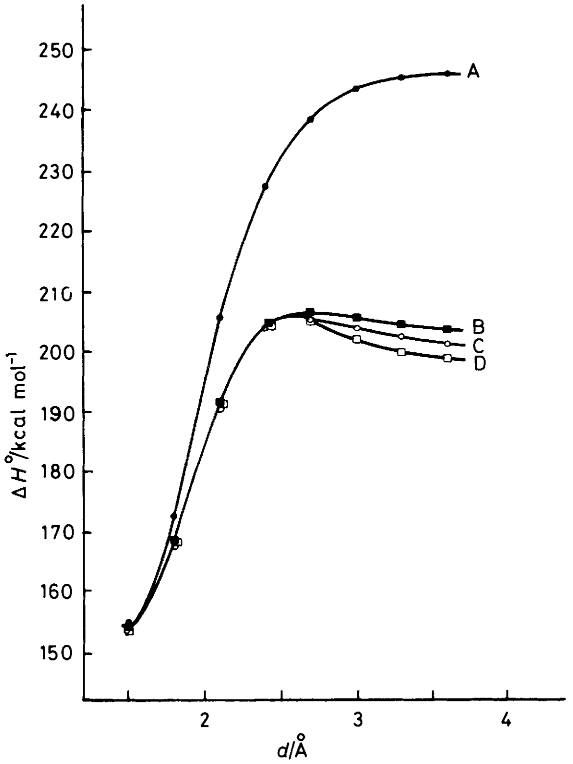
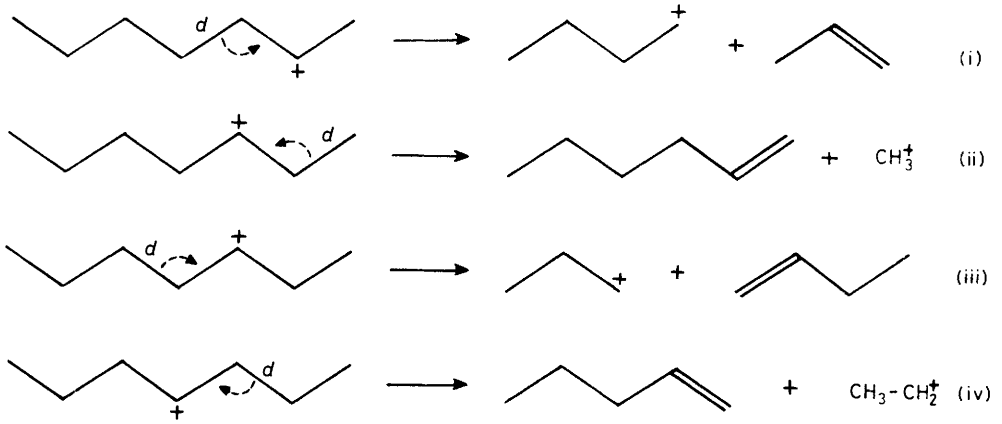


Figure 5. MINDO/3 energy profiles for the β-cleavage of n-heptyl carbenium ions processes. A—D correspond to processes (ii), (iii), (i), and (iv) in scheme 1, respectively



Scheme 1. Simple β-cleavage processes in n-heptyl carbenium ions

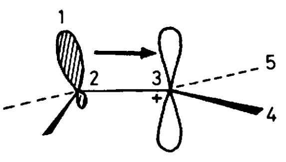


Figure 4. Structural arrangement imposed to the breaking bond (represented by the shaded lobe) and the carbenic vacant AO (unshaded lobes) as the β-cleavage takes place

Rapid rearrangement of primary ions originated in the β-cleavage to yield the more stable secondary or tertiary carbenium ions is generally accepted as a process previous to further β-scission.[1,3]

The least energy consuming rearrangement would be a 1,2-shift of a hydrogen atom.[7] Furthermore, the MINDO/3 electronic population analysis of heptyl ions reveals that an important positive charge is induced over the carbon located with respect to the carbene carbon atom (see Table 2). These facts lead us to consider the possibility of a β-cleavage mechanism concerted with a 1,2-hydrogen shift. In this way, β-

Table 2. MINDO/3 valence electronic population over the carbon atoms in some normal heptyl carbenium ions

	Compounds	
Atoms	3-heptyl	2-heptyl
C(2)	3.930	4.079
C(3)	4.010	3.357
C(8)	3.559	4.023
C(10)	4.032	3.877 *
C(13)	3.878 *	3.930
C(16)	3.917	3.908
C(19)	3.950	3.947

* C located in β in respect to the carbene carbon atom.

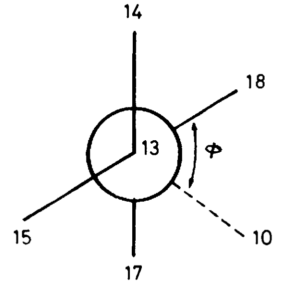
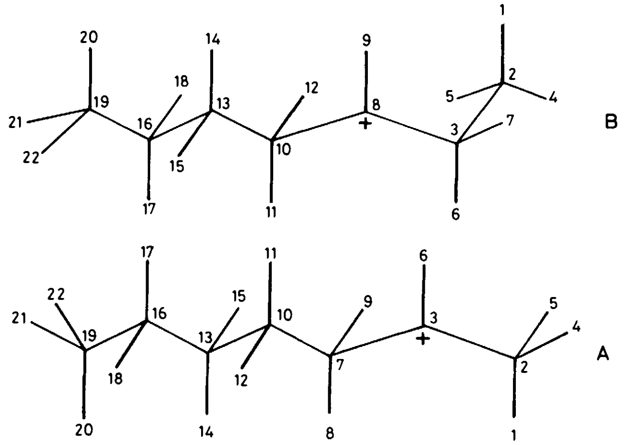


Figure 6. Newman projection of 3-heptyl showing the dihedral angle φ whose value has been fixed to −60, −30, 0, and 180°. The dashed line indicates the cracking bond



Scheme 2. 2-Heptyl (A) and 3-heptyl (B) structures showing the atom numbering

cleavage would yield, in a direct way, α-olefin and a smaller secondary carbenium ion. If such a concerted mechanism produces an appreciable decrease of the barrier height when compared with the simple β-cleavage, considered above, the relative yields of (C_2 + C_5) fractions in relation to (C_3 + C_4) ones would easily be explained because the β-cleavage yielding the C_2 fraction cannot take advantage of the additional stability owing to primary to secondary rearrangement. In other words, a concerted β-cleavage yielding α-olefin and a secondary carbenium ion only can be considered when the separated fraction has three or more carbons.

There are two possible processes of β-cleavage concerted with 1,2-hydrogen shift. They are indicated by reactions (5) and (6).

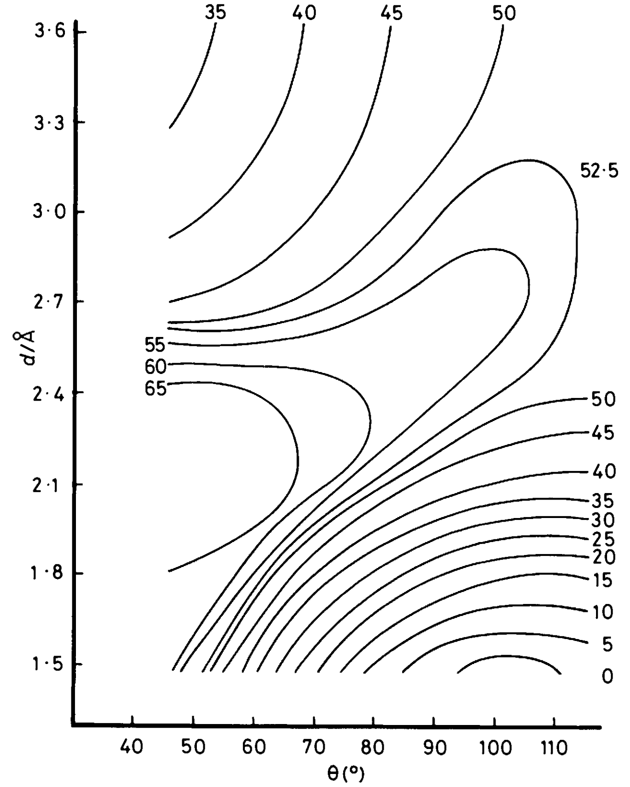


Figure 7. Two-dimensional projection of 3-heptyl β-cleavage energy hypersurface for a value of the dihedral angle φ −60°. See text for details

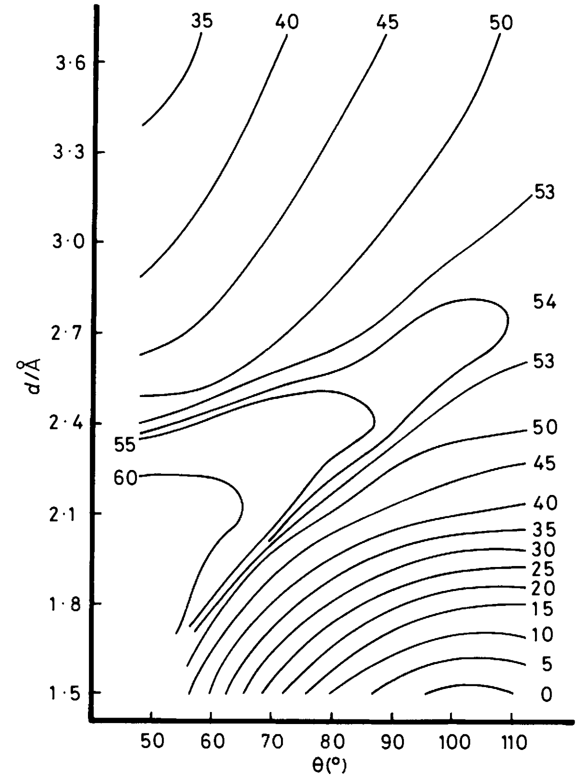


Figure 8. Two-dimensional projection of 3-heptyl β-cleavage energy hypersurface for a value of the dihedral angle φ −30°

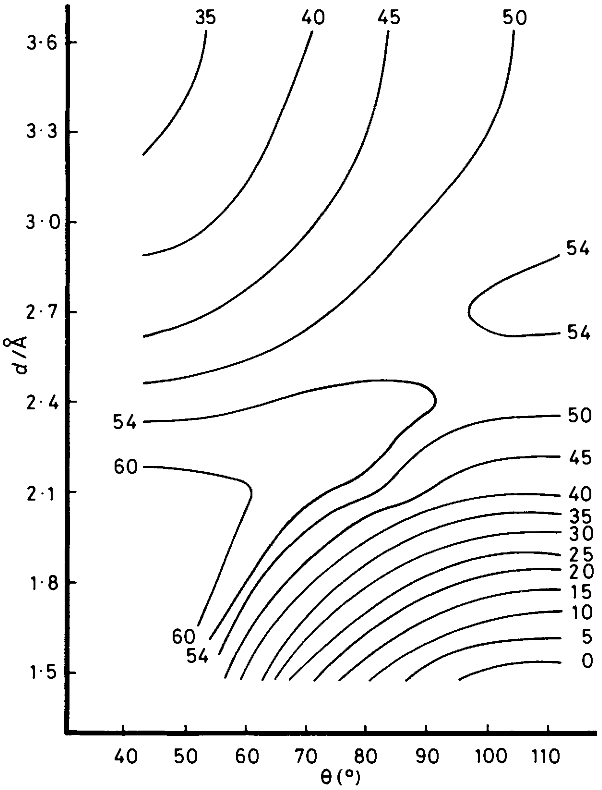


Figure 9. Two-dimensional projection of 3-heptyl β-cleavage energy hypersurface for a value of the dihedral angle φ 0°

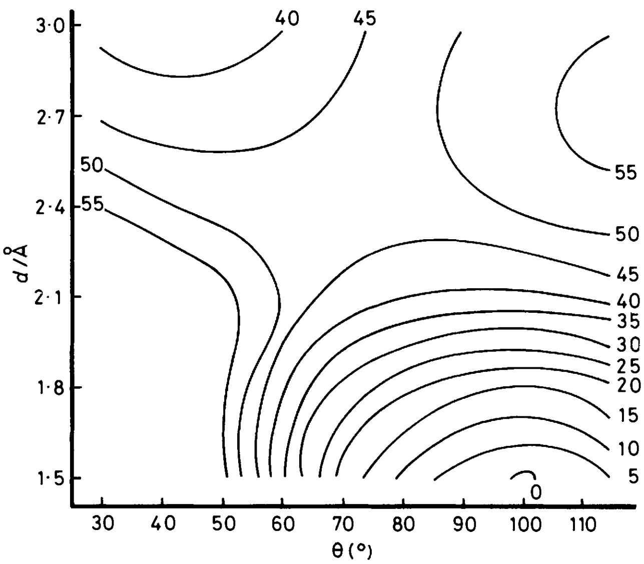


Figure 10. Two-dimensional projection of 3-heptyl β-cleavage energy hypersurface for a value of the dihedral angle φ 180°

$$\text{3-heptyl} \longrightarrow \text{2-propyl} + \text{but-1-ene} \qquad (5)$$

$$\text{2-heptyl} \longrightarrow \text{2-butyl} + \text{propene} \qquad (6)$$

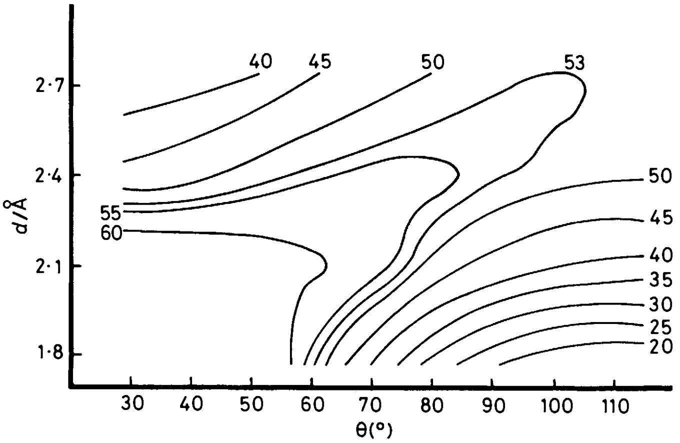


Figure 11. Two-dimensional projection of 2-heptyl β-cleavage energy hypersurface for a value of the dihedral angle φ −30°

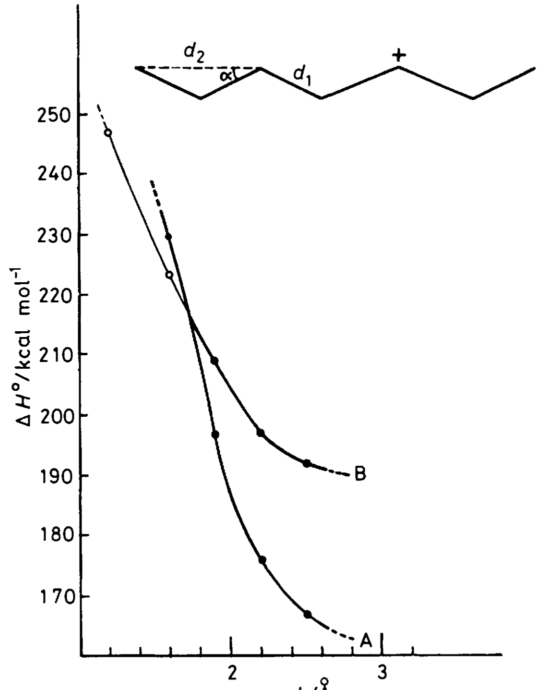


Figure 12. Energy profiles of 3-heptyl hypersurface obtained through a stepwise variation of parameter d_2 for two different values of cracking parameter d_1: (A), d_1 1.8 Å; (B), d_1 2.1 Å

The heptyl ions are shown in Scheme 2 where the numbering is also indicated.

A number of MINDO/3 calculations have been carried out on the 3-heptyl β-cleavage hypersurface. This hypersurface has been reduced to two-dimensional projections for the fixed values of −60°, −30°, 0°, and 180° of the dihedral angle φ, H(18)–C(16)–C(13)–C(10) (see Figure 6). The variation of this dihedral angle could affect the activation energy barrier for a 1,2-hydrogen shift, because it can be associated with a variation of the overlap between the breaking bond [C(16)–H(18)] and the molecular area about C(13) that will remain as charge deficient when the cracking of C(13)–C(10) goes on. The mechanism is concerted in the sense that the 1,2-shift will occur simultaneously with the β-scission (see Figure 6).

The projections have been calculated by scanning two parameters: (1) the distance d[C(13)–C(10)] whose enlargement corresponds to cracking and (2) the angle θ[H(18)–C(16)–C(13)] whose closure is associated with the H(18) shift.

Apart from these parameters and the dihedral angle C(13)–

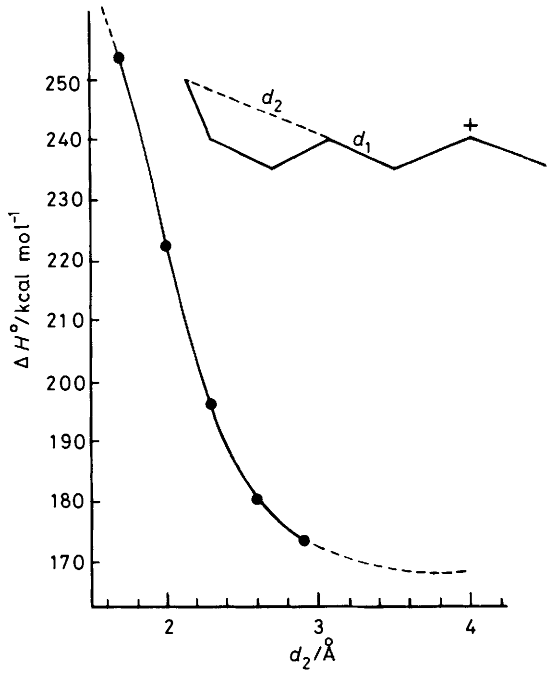


Figure 13. Energy profile of 2-heptyl hypersurface obtained through a stepwise shortening of parameter d_2 for a value of d_1 of 1.8 Å

C(10)–C(8)–C(3), all the rest of the geometrical parameters have been optimized.

The projections are drawn in Figures 7—10. Also for the projection of Figure 10 the maximum of the reaction path has been characterized as a true transition state by diagonalizing the force constant matrix. From Figures 7—10 it can be seen that the influence of the dihedral angle φ on the activation energy is negligible. Also it can be seen that the 1,2-shift only occurs when the breaking of the C–C bond is nearly achieved. In the most advantageous case (φ 180°) the 1,2-shift will occur at C(13)–C(10) distances >2.1 Å and after an energy gain >45 kcal mol^{-1}.

Similar calculations have been carried out for the 2-heptyl carbenium ion. The projection corresponding to a value of the dihedral angle H(15)–C(13)–C(10)–C(7) equal to –30° is shown. Other projections are not included because they do not influence significantly the energy profile.

The results for 2-heptyl (see Figure 11) are very similar to those of 3-heptyl.

From these calculations it follows that our assumption of a concerted β-cleavage plus 1,2-hydrogen shift mechanism does not overcome the difficulties shown by simple β-cleavage.

We have considered, as a further possibility, a concerted process implying isomerization plus cracking that would produce branching rearrangment over the charge-deficient carbon atom placed β to the carbene carbon and simultaneously cracking to give a secondary carbenium ion and an α-olefin.

The generally accepted mechanism for branching rearrangement goes through a protonated cyclopropane ring.[7,30,31] To take account of such a possibility, the energy surface $E\{d[\mathrm{C}(10)\text{–}\mathrm{C}(13)], d[\mathrm{C}(19)\text{–}\mathrm{C}(13)]\}$ was explored for 3-heptyl. The results are shown in Figure 12 It can be seen that an important destabilization takes place when the system is forced to form a ring. This result indicates that the supposed concerted way does not hold.

An additional exploration of the energy surface including the angle α (see scheme in Figure 12) as a third parameter did not improve the results. Hence, they will not be referenced here.

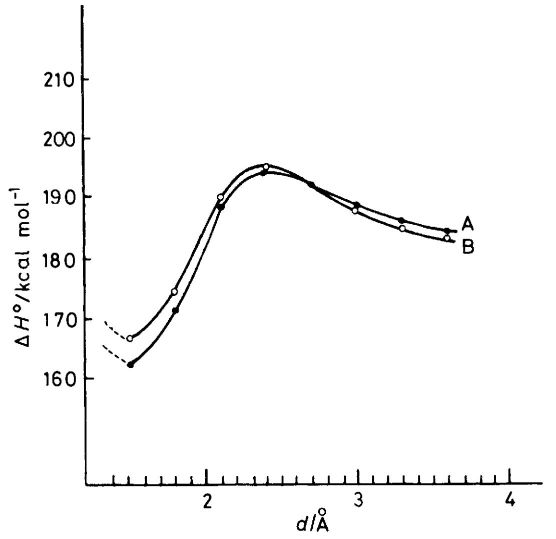
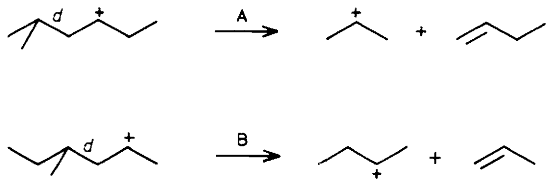
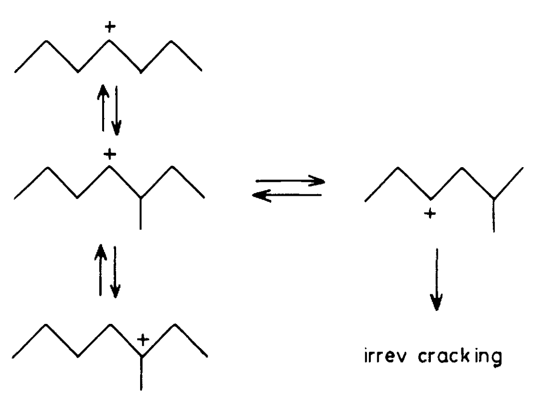


Figure 14. Energy profiles for β-cleavage of 1-ethyl-3-methylbutylium (A) and 1,3-dimethylpentylium (B) carbenium ions



Scheme 3. β-Cleavage processes starting from branched carbenium ions. (A), 1-Ethyl-3-methylbutylium ion, (B), 1,3-dimethylpentylium ion. The symbol d indicates the cracking parameters



On the basis of the results obtained for 3-heptyl, we must refuse the hypothetical protonated cyclopropane mechanism both for 3-heptyl and 2-heptyl ions. However, in the 2-heptyl carbocation another ring-rearranging route can be considered *via* a protonated cyclobutane (see Figure 13). We can suppose that a path going through a transition state with a four-membered ring instead of a three-membered ring would be more favoured because of the less ring strain in the four-membered ring case. To study in a direct way this new possibility of concerted isomerization-cracking we have calculated the energy profile associated with a variation of the length of d_2 using a fixed value of 1.8 Å for d_1 (see Figure 13).

As previously, the coplanarity associated with β-cleavage was forced and the rest of parameters were left to optimize. The results shown in Figure 13 and those discussed above suggest the impossibility of a concerted mechanism that would involve hydrogen or carbon rearrangement plus cracking. We can state that as long as MINDO/3 surfaces were explored and as long as they are reliable, β-cleavage shows similar energy barriers whatever the fraction size.

Up to now we have been concerned with β-cleavage of linear heptyl carbenium ions. It is well know that for branching rearrangements, the experimental transition energies are *ca.* 15—20 kcal mol^{-1}.[7] These values are clearly smaller than our approximate MINDO/3 values for simple and concerted β-cleavage in normal heptyl carbenium ions. So we can suppose that the process of β-cracking starts from previously rearranged carbocations. The validity of this suggestion will be determined by two factors. (1) The values of transition state energies for β-cleavage of branched carbenium ions must be less than that of linear carbenium ions, and (2) a fast equilibrium must be reached between the different isomeric carbenium ions prior to the beginning of β-cleavage. Both conditions can reasonably be postulated from the available experimental data.[7]

We have performed some calculations in order to analyse whether the energetic differences between the transition states for β-cleavage starting from linear or branched carbon chains are large enough to account for the yield pattern of the experimental products.[11,12]

The MINDO/3 energetic profiles for the β-cracking of 1-ethyl-3-methylbutylium and 1,3-dimethylpentylium ions are shown on Figure 14. For B profile the maximum has been characterized as a saddle point by diagonalizing the force constant matrix. Then a similar situation has been accepted for the maximum of profile A.

As can be seen, the barrier height for the processes shown in Scheme 3 is estimated by MINDO/3 to be *ca.* 30 kcal mol^{-1}, which represents 20 kcal mol^{-1} less than the height estimates for n-heptyl β-cracking, and an intermediate value between the experimental values found for branching rearrangement and MINDO/3 values for linear chain β-cracking.

Consequently, we conclude that a plausible mechanism for cracking implies a rapid achievement of the equilibrium between different carbocations after the hydride transfer carbenium ion generation, and then the irreversible β-cracking that would shift the equilibria to the right. There is no way of obtaining a (C_2 + C_5) fraction through such a mechanism, the less favourable direct β-cleavage being the only way to obtain it. This result is in good agreement with the reported experimental results for heptane as indicated above.[11,12]

A realistic study of linear carbenium isomerization mechanism (branching rearrangement) and energy barriers must go through extensive calculations of the three-membered ring intermediate proposed by Brouwer.[7] Up to now, some accurate calculations have been performed on the protonated cyclopropane ion energy surface (see Table 1). On the basis of the results of Pople *et al.*[20] and Kohler and Lischka[21], the energy difference between protonated cyclopropane and 2-propyl carbenium ion is *ca.* 20 kcal mol^{-1} (SCF only) or <10 kcal mol^{-1} (when correlation energies are considered). Our MINDO/3 results are in good agreement with the last result. All those values lead us to propose, as a possible mechanism of n-heptane cracking, isomerization and further β-cleavage.

In conclusion, it is shown that direct β-cleavage or a concerted mechanism or cracking *via* protonated cyclopropane or protonated cyclobutane cannot fully explain the observed experimental facts such as activation energy and product distribution. We propose as a possible and more favourable mechanism for the n-heptane cracking, isomerization, and further β-cleavage. This process would take place together with the less favourable direct β-cleavage. We believe that the conclusions obtained for heptane can be applied to the cracking of higher hydrocarbons.

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