

An Analysis of Factors That Influence Shape Selectivity in the Cracking of Long-Chain Alkanes on Zeolite Catalysts

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The method and equations previously developed for conformational analysis of linear alkanes are used to calculate the free energy differences between heavily coiled (four *gauche* bonds or more) and extended forms. Since a *gauche* bond is similar in its steric requirements to a methyl side chain, it follows that chain straightening is a required step (preequilibrium) for the reaction of linear alkanes inside the channels of small- and medium-pore zeolites. Any energy advantage from attractive van der Waals interactions with the walls of the channels can be gained only after the chain uncoils. For a 20-carbon chain the preequilibrium retards the reaction inside the pores relative to that on the external surface by at least four powers of ten. Two other factors acting in the same direction are a requirement for proper orientation to enter the channel (worth one order of magnitude for C₂₀) and the retarding effect of constraining a molecule inside the channel on the cracking reaction itself. The observed selectivities require either that the intrinsic activity of sites within channels be many orders of magnitude higher than that of sites on the external surface, or that the normal alkanes reacting in the coiled form have an intrinsically higher reactivity toward cracking than the branched isomers, and the reactions occur predominantly on the external surface of the zeolite crystal for both types of chains. © 1990 Academic Press, Inc.

I. INTRODUCTION

Preferential cracking of linear alkanes in mixtures with their branched isomers has been reported on small-pore (1) and medium-pore zeolites (2). Such a substrate discrimination has been explained by the concept of shape selectivity (3), which considers that the locus of catalysis for the conversion of alkanes is the interior of the zeolite channels. According to this model the zeolite exhibits selectivity when the size of its channels matches the size of the normal chain (actually the van der Waals diameter of the latter) (3), or the size of the activated complex for the conversion of the straight chain (3c). It is generally considered that a medium-pore zeolite like ZSM-5 accepts and cracks within its channels a

normal or monomethyl-substituted alkane, but it excludes a dimethyl-substituted chain (3c).

Discrimination by size is well understood for equilibrium processes; it is the basis of the molecular sieve effect of zeolites. Cracking on zeolites was introduced, however, to achieve selective removal under kinetic control of *n*-alkanes from a mixture (1), with the understanding that the selectivity is determined by the locus of reaction: on the exterior of the crystal for branched isomers, inside the channels for the linear ones. In the present paper we present theoretical arguments that indicate a very strong bias for linear chains toward reaction on the exterior surface of the zeolite crystal, rather than inside the channels. Three factors determining this preference are discussed, in the order of the importance of their contribution to this preference: the conformational preequilibrium existing for the reaction inside the channels, the orientation of the reactant mole-

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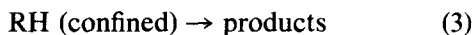
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cule colliding with the solid surface, and the mechanism of the cracking reaction.

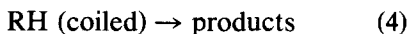
II. THE CONFORMATIONAL PREEQUILIBRIUM

For the analysis of a kinetically controlled process it is not important whether a molecule from the fluid phase in equilibrium with the zeolite prefers a certain location, but whether the overall rate for the reaction occurring at that location is greater than the rate of the reaction taking place in another region of the catalyst. In the consideration of reaction rates inside the zeolite channels, the conformation and the conformational changes of the reactant molecule at the reaction temperature are important.

For any chain of four carbon atoms the central bond can exist in two types of conformation: *anti* and *gauche*. As pointed out previously (4), a linear alkane is admitted in the channel in its extended, all-*anti* conformation (5). In terms of space requirements the existence of a *gauche* conformation along the chain is similar to the existence of a methyl branch (4). Presence of more *gauche* bonds has a greater effect than the presence of an equivalent number of methyl substituents, since the chain folds upon itself. Therefore, the *gauche* conformations should uncoil before entering to react within the channels. Any energy advantage from attractive van der Waals interactions with the walls of the channels (5) can be gained only after the chain uncoils. The overall reaction within the channels is described by



in which the cracking itself is preceded by the conformational equilibrium and by the diffusion into the channel. The reaction on the external surface of the catalyst



does not require any readjustment of conformation (or diffusion into the crystal, for that matter). The coiled chain can interact sideways with the active centers.

The equilibrium constant for Eq. (1), $K = [\text{all-anti}]/[\text{coiled}]$, enters as a factor in the overall rate constant for the conversion of normal alkanes inside the zeolite channels:

$$k_{\text{int}} = k'_{\text{int}} K. \quad (5)$$

By contrast, the rate for the reaction occurring on the outside surface

$$k_{\text{ext}} = k'_{\text{ext}} \quad (6)$$

is not affected. In Eqs. (5) and (6), k are the measured rate constants, k' are the intrinsic rate constants on the active sites, and the subscripts "int" and "ext" refer to the interior (channel) surface and exterior surface, respectively. For a complete treatment, the effect (also retarding) of Eq. (2) upon k_{int} may be introduced as well in Eq. (5).

The value of K is obtained from the free energy differences between the conformers. As discussed previously (4) the steric energies obtained by molecular mechanics calculations (6-8) are a good measure of the enthalpy differences, whereas the entropy differences are determined statistically by the number of conformers that have the same steric energy. To deduce K it is necessary to count all the conformers and to evaluate their relative steric energy (differences in strain).

A detailed conformational analysis of straight chains was presented elsewhere (4). A summary of the results of that work is given in the Appendix. It is found, for instance, that the coiled forms of hexane are preferred by 2.9:1 at 400 K and by 4.9:1 at 550 K.⁴ This variation comes from the fact that the extended form is favored by enthalpy and coiled form by entropy, which becomes the dominant factor at higher temperature.

⁴ The values obtained without the symmetry correction of entropy [2.0:1 and 2.9:1, respectively (4)] were too low.

For the evaluation of shape selectivity, the conformers with two or more *gauche* bonds ($i > 2$ as defined in the Appendix), equivalent to molecules with two methyl branches or more, should be considered. We chose, however, a more stringent case, and calculated the free energy differences between the all-*anti* conformer on one side and the forms with $i = 4$ and higher on the other side. We note that these coiled chains are equivalent in their steric requirements to heavily branched isomers: a hydrocarbon with four methyl branches, 2,6,9,14-tetramethylpentadecane (pristane), is generally considered a prototype of highly branched alkanes.

The value of K for the preequilibrium [Eq. (1)] is temperature dependent. The interval indicated in publications dealing with processes for selective conversion of straight-chain alkanes is 450 to 950°F (1, 2c). We chose for our evaluation a temperature at the lower end of that interval, 550 K (530°F). The free energy differences between the conformers with $i > 4$ and the all-*anti* conformers at that temperature are represented as a function of the size of the alkane in Fig. 1. The correlation starts with heptane, the shortest chain that can have four *gauche* bonds.

From Fig. 1 it can be seen that already for undecane, the heavily coiled conformers are favored over the all-*anti* form by 4.4 kcal/mol. For a 20-carbon chain this preference should be in excess of 10 kcal/mol, which translates into a rate factor of about 10,000 retarding the reaction inside the channels (after uncoiling of the alkane chain) relative to the reaction of the coiled alkane on the external surface of the zeolite crystal, at 550 K. At higher temperature this preference is more pronounced. Moreover, as indicated in the Appendix, the free energy preferences for coiled isomers shown in Fig. 1 are actually too low.

Selective conversion of normal alkanes significantly larger than C_{20} is sought or claimed in some industrial processes (1, 2c). For chains of such lengths the barrier which the conformational preequilibrium

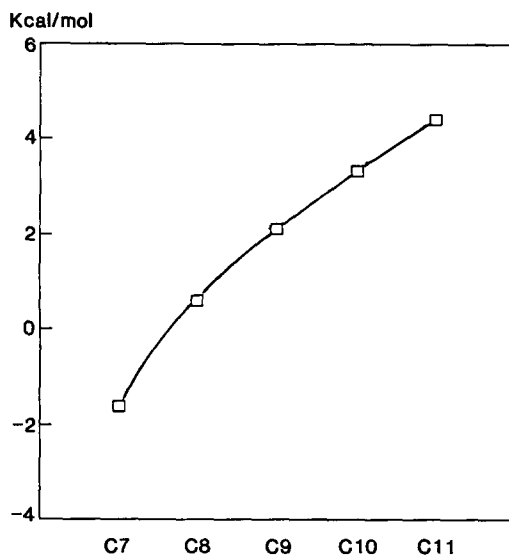


FIG. 1. Free energy differences between coiled ($n \geq 4$) and all-*anti* forms of normal alkanes.

places before conversion inside the channels should be enormous.

III. ORIENTATION OF THE REACTANT MOLECULE COLLIDING WITH THE SOLID SURFACE

To react, a molecule from the gas phase has to collide with the catalyst surface. It has been discussed in the literature that the orientation of the reactant molecule relative to the pattern of distribution of active sites on the catalyst surface can determine the rates and selectivities of catalytic reactions; the term of landing area was proposed (9).

Similar constraints exist in the case discussed here. The alkane molecule can enter a pore if it arrives at the pore opening. If it comes into contact with the surface between pores, it can react on an acid site present in a five- or six-membered ring on the surface of the crystal. The relative probability of the two events is determined by the structure and geometry of the catalyst particle. For a hexagonal distribution of pores (10), a pore diameter of 5.4 Å (11), and a distance between the centers of two adjacent pores of 8 Å, the ratio of pore opening area to the remainder of the external surface area (small rings) is 1:4.

On the other hand, even when a molecule of *n*-alkane "lands" on a pore opening, it can enter the channel only if the end of the chain faces the pore. Otherwise it has to sit on the landing spot until it reorients itself, or is converted by an acid site existing at or near the pore opening. The chain orientation effect reduces the rate of reaction within the channels relative to the reaction on the exterior of the crystal by a factor which increases with the chain length. It can be approximated by the ratio between the number of methylene groups and the number of methyl groups in the chain, that is, 1/5 for dodecane (two methyl groups and 10 methylene groups), 1/9 for a 20-carbon chain (eicosane), and 1/19 for a 40-carbon chain.

It is possible that there is a reservoir of adsorbed molecules on the surface and within the pores.⁵ This pool being at steady state, however, the rate-determining step of the overall reaction is not changed. The entropy-governed preference for the coiled forms at high temperatures exists in the liquid phase as well as in the gas. Therefore, the retarding effect of both the conformational preequilibrium and the orientation of the reactant molecule on the surface should still be manifested.

Another possibility is that the interaction energy of the hydrocarbon with the crystal surface is stronger than the van der Waals interactions and this interaction with the surface could lead to uncoiling.⁵ Such a stronger interaction, however, would be a polar interaction, and should lead to catalytic conversion on the surface. Even though some selectivity might be manifested by the pore opening area of the crystal (12) it is not of the type that discriminates against branched or coiled chains.

IV. MECHANISM OF THE CRACKING REACTIONS

Two mechanisms, differing by the nature of the rate-determining step, were proposed

a few years ago for the cracking of alkanes on zeolites (13). (a) At lower temperatures (e.g., 623 K) the rate-determining step was said to be the hydride transfer between a carbocation and a hydrocarbon molecule, followed by cracking in a fast step. (b) At higher temperatures (723 K and above) the cracking step becomes rate determining, and is preceded by a fast preequilibrium involving only the catalyst and a molecule of substrate.

For mechanism a, it has been established (14) that hydride transfer is sterically demanding and requires proper orientation of the species that exchange the hydride. Transfer between two secondary positions would require distortions of the donor and acceptor chains that the narrow pores can hardly accommodate. In case b, the cracking step, which has a positive activation entropy and activation volume, should be slower in the strictly confined state of the chain in the channel than on the external surface. Besides, mechanism b prevails at temperatures at which the effect of the conformational preequilibrium (*K* above) is exceedingly high.

We do not think that the proposed departures (13) from the normal mechanism of catalytic cracking have been satisfactorily demonstrated.⁶ The general mechanism of cracking on catalysts that promote carbocationic reactions consists of a rate-determining reaction between the catalyst and substrate, followed by a reaction chain of cracking and hydride transfer steps (15). Even for the general mechanism, however, the retarding effects of confinement inside the channels on hydride transfer and cracking steps should reduce the overall rate by shortening the reaction chain. The diffusion limitations [Eq. (2)] also represent a serious impediment to a chain reaction within the channels. No such adverse effects exist for the reaction on the outside surface.

⁶ Reactivity differences at temperatures as high as 811 K were reported in Ref. (3c) and assigned to steric constraints on the "bulky bimolecular transition state."

⁵ Suggested by a reviewer of the manuscript.

In any case, the effect of the cracking reaction mechanism on selectivity should be the least important factor, since the conformational preequilibrium and, to a far lesser extent, the orientation requirement for penetration into the pores should essentially determine the preference for reaction of *n*-alkanes on the exterior surface.

V. CONCLUSION

The importance of conformational effects in catalysis was long understood qualitatively. A quantitative evaluation of these effects in reactions of *n*-alkanes was made possible by the development of the method and equations for counting of conformers (4). We found that conformational energies become overwhelming for long chains.

As mentioned in the Introduction, molecular sieve effects in equilibrium processes on small- and medium-pore zeolites are still expected at the temperatures discussed here (550 K). At higher temperatures, the entropy effects should control the entire process, and equilibrium molecular sieve effects should vanish. Thus, from a method based on equilibration of a zeolite with a flow of hydrocarbons diluted with He, it was found that at steady state the ratio of *n*-hexane to 3-methylpentane in the pores of ZSM-5, in equilibrium with a 1 : 1 mixture of the two in the gas flow is 28 at 293 K, but only 4 at 403 K. The variation is due mostly to the decrease in the amount of the linear isomer in the pores (16). This is understandable, because the branched isomer has fewer conformations available and its conformational energy is, therefore, less temperature dependent (4). From the published results (16) one can predict that at higher temperatures, the amount of linear isomer in the pores should be zero.

Cracking on zeolites was introduced to achieve selective removal of *n*-alkanes under kinetic control (1). Our analysis argues strongly against the existence of a kinetic molecular sieving effect at any temperature substantially higher than room temperature. There is no question, however, that

ZSM-5 does crack *n*-alkanes preferentially, whereas H-Y, for example, does not show such a selectivity. Therefore, other possible causes of the observed selectivity for conversion of straight-chain alkanes over their branched isomers should be seriously considered:

1. *Selectivity is determined by the ratio of internal to external surface of the zeolite.* Despite the bias of *n*-alkanes toward reaction on the external surface of the crystal, their cracking could take place predominantly inside the channels if the internal (channel) surface area were larger than the external crystal surface by a factor significantly greater than the numbers that can be derived from Sections II–IV (at least 10^5 for C₂₀). The relative contribution of active sites on the external and internal surface of zeolites has been discussed in the literature (17, 18)⁷; the internal to external surface area ratio required to produce the selectivities reported for alkane cracking (1–3) would be achieved for 3- to 5-mm individual crystals (18). It turns out, however, that in the applications that concern us here, the opposite tendency has been manifested. Zeolites with crystal sizes of 100 Å or less are made and employed industrially (19). Thus, the selectivity cannot originate in the ratio of internal to external areas.

2. *Chain uncoiling and channel penetration are concerted.* A molecule that satisfies the orientation requirement (cf. Section III) can be visualized as slowly penetrating the channels as it unwinds. In this case, (a) most of the reactions should occur on the sites outside and around the pore openings, or in a layer 5–7 Å thick; (b) the catalyst should not be more selective for long straight-chain molecules than for branched chains with linear ends or side chains of five or six carbon atoms. As an example, nonane, which can penetrate with both ends into the channels, could be no more than

⁷ This possibility was discussed for the discrimination between *n*-alkanes and dimethyl-substituted alkanes in Ref. (3c).

twice as reactive as 2,2-dimethylheptane, which can penetrate only with one end of the chain. This prediction is at variance with the experiment (3c).

3. *The intrinsic activity of a site inside the channel is higher than that of a site on the exterior surface by many orders of magnitude.* At this time, however, there is no experimentally established structural feature of zeolites that substantiates such a behavior. One should note that the nature of active sites does not differ in the interior from the exterior of crystals. Any crystal grows by the deposition of material from solution on a surface (20). In the case discussed here, the template cations are deposited on the surface and the cages or channels grow around them.

4. *The reactions of both branched and linear long-chain alkanes occur largely on the external surface.* The selectivity should then originate in a higher intrinsic reactivity of the linear chains (reacting in the coiled form) on the zeolite surface. Observed differences in selectivity between medium- and large-pore zeolites should then be produced not by the size of the channels, but by other factors. There is no need to emphasize that differences in pore size between different types of zeolites always come together with other chemical and structural differences, such as number, nature, and strength of acid sites and intervention of one-electron transfer mechanisms. This aspect of the structure-reactivity relationship for zeolite catalysts certainly warrants more extensive investigation.

Of the alternatives considered, the first is the least probable. Whatever our preference may be among the other possibilities, a clear-cut choice cannot be made by theoretical modeling alone. Some experiments could test our hypotheses⁵:

—Maintain Al content and distribution constant and vary the crystal size.

—Maintain the crystal size constant and vary the Al content.

—Modify the Al concentration gradient of crystals of equal size by enriching and by depleting the crystal surface of aluminum.

Other experimental approaches can be conceived as well, and we are currently investigating some of the possibilities. Other researchers, perhaps better equipped than us, might find the pursuit of these questions interesting.

APPENDIX

The number of conformational isomers (rotamers) of an alkane was calculated (4) as a function of the chain length expressed by the parameter n (number of relevant bonds, equal to the number of carbon atoms of the chain minus 3):

$$\text{For even } n \ (n = 2m), \\ N = 3^m(3^m + 1)/2. \quad (7)$$

$$\text{For odd } n \ (n = 2m + 1), \\ N = 3^{m+1}(3^m + 1)/2. \quad (8)$$

Thus, butane ($n = 1$) has 3 conformers (rotamers), dodecane ($n = 9$) has 9963, hexadecane ($n = 13$) has 798,255, eicosane ($n = 17$) has over 64.5 million, etc.

Also the number of rotamers with a given count of *gauche* bonds, i , in a straight chain with n relevant bonds was obtained as

$$r_n^i = \frac{1}{2} [{}^n_i] \times 2^i + \frac{1}{2} r_n^i \quad (9)$$

in which $[{}^n_i]$, “ n chooses i ”, indicates in how many ways i *gauche* bonds can be placed in n “slots” (relevant bonds). It can be expanded as $n!/i!(n-i)!$

The correction term, r_n^i , is zero for a combination of n even and i odd. In all other cases it is given by

$$r_n^i = \left[\frac{\text{int}\{n/2\}}{\text{int}\{i/2\}} \right] \times 2^{\text{int}\{(i+1)/2\}} \quad (10)$$

where $\text{int}\{. . .\}$ means the integer part of the fraction.

From these equations we found, for instance, that decane (maximum number of *gauche* bonds possible $i = n = 7$) has 146 conformers with $i = 3$, 286 conformers with $i = 4$, 348 conformers with $i = 5$, 228 con-

TABLE 1
 Steric Energy Increments per *gauche* Bond (kcal/mol)

Alkane	<i>n</i>	0 <i>g</i> → 1 <i>g</i>	1 <i>g</i> → 2 <i>g</i>	2 <i>g</i> → 3 <i>g</i>	3 <i>g</i> → 4 <i>g</i>	4 <i>g</i> → 5 <i>g</i>	5 <i>g</i> → 6 <i>g</i>	6 <i>g</i> → 7 <i>g</i>	7 <i>g</i> → 8 <i>g</i>
Pentane	2	0.90	0.72						
Hexane	3	0.91	0.76	0.64					
Heptane	4	0.90	0.78	0.63	0.68				
Octane	5	0.90	0.81	0.65	0.59	0.74			
Nonane	6	0.89	0.82	0.70	0.59	0.58	0.77		
Decane	7	0.90	0.83	0.72	0.60	0.56	0.59	0.82	
Undecane	8	0.90	0.83	—	—	—	—	0.67	0.83

formers with $i = 6$, and 72 conformers with $i = 7$. For the not much longer chain of tridecane ($n = 10$), there are 480, 1700, 4032, 6760, 7680, 5800, 2560, and 528 conformers with 3, 4, 5, 6, 7, 8, 9, and 10 *gauche* bonds, respectively (4).

The actual list of rotamers of each normal chain can be generated by a simple procedure, which can be adapted for the computer.

The determination of steric energies (*SE*) and heats of formation (ΔH_f^0) by molecular mechanics is well established (6, 7). In particular for alkanes the results are quite accurate. We established that the steric energy differences between the all-*anti* and coiled forms of alkanes can be described in terms of a few characteristic elements of conformation present as alterations from the all-*anti* chain. The energy increments for those elements of conformation were obtained by calculating (6, 8) the steric energies for 552 individual conformers. We have since checked and refined the increments by calculating likewise the steric energies for more than 1000 additional conformers, thus covering all the conformers of the group from pentane to decane. In addition, 177 selected conformers of undecane were calculated. The steric energy increments for the four basic elements of conformation of alkanes obtained from these calculations are listed in Tables 1–4. As observed previously (4), the increments tend to decrease with the increase in chain

length, in some cases tending toward some limiting values. The increments listed can be used to obtain the steric energies and heats of formation of the conformers of alkanes with much longer chains.

The other component of free energy, entropy, is determined (4) for each group of coiled rotamers as $R \ln(q_n^i)_{SE}$, where $(q_n^i)_{SE}$ is the number of rotamers that have the same values for n , i , and *SE*. The groups are determined by the elements of conformation for which steric energy increments were calculated as discussed above. The entropy for each conformer has then to be corrected on the account of symmetry (21).⁸ It is seen immediately that the extended (all-*anti*) form and those coiled forms that have their *gauche* bonds distributed symmetrically relative to the central atom or bond possess a twofold symmetry axis, passing through the central carbon ($n = 2m$) or through the central bond ($n = 2m + 1$). The correction is most conveniently made by counting all other rotamers twice. The numbers used to generate Fig. 1 of this paper are symmetry corrected.

Another correction to be considered accounts for the existence of two energy minima for the chains with two consecutive *gauche* bonds with torsional angles of opposite sign, g^+g^- [helix inversion (4)]. We

⁸ This correction was discussed in Ref. (4), but for the sake of expediency, it was omitted from the numbers used to generate Figs. 1 and 2 therein.

TABLE 2
Steric Energy per Helix Inversion (g^+g^- element) (kcal/mol)

Alkane	n	i	First inversion	Second inversion	Third inversion
Pentane	2	2	1.61		
Hexane	3	2	1.55		
		3	1.64		
		4	1.51		
Heptane	4	2	1.51		
		3	1.65		
		4	1.71	1.09	
Octane	5	2	1.45		
		3	1.55		
		4	1.66	1.30	
		5	1.75	1.27	
Nonane	6	2	1.44		
		3	1.51		
		4	1.57	1.42	
		5	1.69	1.35	
Decane	7	2	1.41		
		3	1.47		
		4	1.52	1.37	
		5	1.60	1.39	
		6	1.73	1.42	1.54
Undecane	8	2	1.39		
		3		1.43	1.24
		4		1.82	
		5		1.83	
		8			

TABLE 3
Steric Energy Increments per $g^+g^-g^+$ Sequence (kcal/mol)

Alkane	n	i	First occurrence	Added to g^+g^-	Second occurrence
Hexane	3	3	3.28		
Heptane	4	3	3.13		
		4	3.55		
Octane	5	3	2.94		
		4	3.37		
		5	3.81	2.61	
Nonane	6	3	2.80		
		4	3.16		
		5	3.63	2.96	
Decane	7	3	2.63		
		4	2.98		
		5	3.39	2.94	
		6	3.82	2.96	2.40
Undecane	8	7	4.03	3.19 ^a	2.50
		8	4.02		

^a Added to two g^+g^- groups: 2.59.

TABLE 4
Steric Energy Increments per g^+ag^- group (kcal/mol)^a

<i>n</i>	<i>i</i>	No g^+g^- present		One g^+g^- present		Two g^+g^- present ^b	
		First g^+ag^-	Second g^+ag^-	First g^+ag^-	Second g^+ag^-	First g^+ag^-	Second g^+ag^-
3	2	0.23					
4	2	0.25					
	3	0.29		0.18			
5	2	0.23					
	3	0.29		0.20			
	4	0.34		0.21	0.48		
6	2	0.23					
	3	0.29	0.28	0.17			
	4	0.31	0.30	0.26	0.28	0.45	
	5	0.36		0.26		0.37	
7	2	0.21					
	3	0.28	0.27	0.16			
	4	0.32	0.32	0.28	0.29	0.38	
	5	0.36	0.30	0.29	0.28	0.39	0.28
	6	0.41		0.32		0.32	
8	2	0.21					
	6	0.36					
	7	0.41					

^a An average value of 0.3 kcal/mol in all cases was used for this interaction in Ref. (4).

^b No extra strain is introduced by the g^+ag^- sequence in the presence of a $g^+g^-g^+$ group or of three g^+g^- groups.

have established by calculations on the corresponding conformer of pentane that the two forms (torsional angles $+94^\circ$, -62° and $+62^\circ$, -94°) interconvert over an energy barrier (saddle point) by bond rotation⁹ and, therefore, should be counted separately. For more complex sequences of *gauche* bonds, however, one would have to calculate steric energies and, occasionally, check the energy barriers extensively, so we gave up on this correction; taking it into account increases the thermodynamic preference of the coiled conformers over the extended ones, and makes the case for the external surface of the zeolite crystal as the preferred site for the cracking of normal alkanes stronger than indicated by Fig. 1.

Summation over all the coiled forms, from $i = 1$ to $i = n$, gives the extent of their

preference over the all-*anti* form. As discussed in the text, the free energy values in Fig. 1 were obtained by summation over the forms with i from 4 to n .

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