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The Protolysis of Hexanes over a USHY Zeolite

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Detailed information gathered on the cracking of five hexane isomers has revealed major differences in the mechanisms of cracking in the individual isomers and suggests the possibility that synergistic effects play a role in the cracking of mixtures of hydrocarbons. We find that both *n*-hexane and 2,2-dimethylbutane do not crack via the chain process to any significant extent, presumably due to the absence of tertiary hydrogens in both molecules. On the other hand, 2,3-dimethylbutane, with two tertiary hydrogens, cracks readily via a chain process. The two monomethyl pentanes illustrate the fact that tertiary hydrogens are not all the same in terms of reactivity. 3-methylpentane has a much more reactive hydrogen than 2-methylpentane, with the result that more of this feed is converted by chain processes. However, the *overall rate* of conversion is higher in 2-methylpentane and lower in 2,3-dimethylbutane. It seems that, when it comes to maximizing the overall rate of reaction, the dominant influence is the rate of initiation by protolysis. In this work we examine the initiating protolysis reactions of the partent hexane molecules. These reactions start the chain processes which, in various measures, are responsible for the observed overall conversion in "catalytic cracking." We find that the rates and modes of the various protolysis reactions are profoundly different in the five isomeric hexanes. In discussing this fact we raise the issue of the significance of "test reactions" in catalyst evaluation.

INTRODUCTION

This work uses the cracking of hexane isomers to examine the differences which arise in the cracking process when molecular configuration alone is changed. C_6 paraffin cracking selectivity data available from the literature, together with new data reported here, has been interpreted in terms of fundamental elementary processes, yielding:

(a) parameters we call reaction path probabilities (RPPs); and

(b) the individual rates of protolysis reactions (IRRs) in all the C_6 paraffin isomers.

In the following work we use these fundamental measures to examine the influence of molecular structure on:

(a) the initiating protolysis reactions in each case;

(b) on the mechanism of catalytic cracking in each molecule; and

(c) on the relative refractoriness of the five isomeric species.

THEORY AND RESULTS

Well-defined *initial* selectivities must be used in evaluating the fundamental aspects of cracking reaction mechanisms, to avoid confusing the influence of secondary reactions with the initial processes which occur in the overall process of "cracking" in hydrocarbons. These initial selectivities are best obtained by measuring the slopes at the origin of selectivity plots (OPEs), as described elsewhere (1). The OPEs in turn are curves defining the limits of selectivity at each conversion and are obtained by plotting experimental yields of products against the corresponding conversion (1). The initial molar selectivities of the products of protolysis, lumped together with identical products from chain propagation, for the cracking of various hexanes are mostly taken from the literature (2–6), and are presented in Table 1. To interpret this data and see the effect of molecular configuration on the yields of these products due to elementary protolysis (i.e., initiation) reactions alone, we first need to identify candidate protolysis reactions in the cracking of hexanes in general. These are shown in Table 2, which lists all the possible bond scissions in the C_6 molecule except for the reaction which leaves a C_1 carbenium ion on the surface. We believe this latter reaction is unlikely to occur and have found its RPP to be zero in cases where we have attempted to introduce such a process in quantifying our results.

Our experiments were carried out in a fixed bed, plug flow, glass reactor at atmospheric pressure and the temperatures indicated in Table 1. No diluents or carrier gases were used. The catalyst used in all cases was the same pure USHY, made by exchanging a commercial Y zeolite 10 times with 0.5 *M* NH_4NO_3 solution at 20°C, for 24 h per exchange, drying at 110°C for 24 h and then calcining

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TABLE 1

Initial Total Molar Selectivities of Small Paraffins Formed in the Cracking of Hexanes

	n-C_6 (2)	2 *M* C_5 (3)	2 *M* C_5 (3)	3 *M* C_5 (4)	2,3-DMC_4 (5)	2,2-DMC_4 (6)
Product	500°C	400°C	500°C	400°C	400°C	500°C
H_2	0.000	0.0129	0.0989	0.1133	0.0301	0.000
Methane	0.000	0.0145	0.0167	0.0575	0.0215	0.319
Ethane	0.0682	0.0049	0.0086	0.0507	0.000	0.0416
Propane	0.651	0.1801	0.4248	0.3469	0.0360	0.152
Butanes	0.135	0.1124	0.1538	0.1115	0.0427	0.1484
Total	0.8542	0.3248	0.7028	0.6699	0.0943	0.634

after each exchange at 500°C for 2 h. After the 10 exchanges the catalyst was steamed at 200°C for 24 h. The final preparation contained no heteroatom impurities. All products were identified by GC/MS and analysed by capillary chromatography (for liquids), or using a Carle gas chromatograph (for the gases), as described in the publications cited.

As explained in previous work (3), our approach assumes that, after initiation, the cracking of alkanes proceeds to some extent via a set of chain propagating reactions. Thus product paraffins may arise by a protolysis of the original feed molecule (an initiation reaction) or due to a disprorpotionation between a surface carbenium ion and a feed molecule (a chain propagation reaction). The initial selectivities reported in Table 1 are therefore composed of products made by the protolysis of the parent molecule and those made by chain propagating reactions. Each of these modes of feed conversion, be it by an initiation reaction or by a chain propagation reaction, is assigned a probability of taking place at low conversion (in the limit, at zero conversion). This we call a reaction path probability (RPP), designated by an X with two subscripts, so that X_{0i} represents the RPP for the mode of initiation where the pristine Brønsted site causes a paraffin containing i carbon atoms to be protolysed off a feed molecule containing n carbon atoms. X_{ji} represents the probability of conversion of a feed molecule containing n carbon atoms by means of a bimolecular reaction with a carbenium ion of length j. Here, a negatively charged moiety of length i is transferred from the feed molecule to the adsorbed carbenium ion to produce a gas phase paraffin of length $i + j$, leaving behind a postively charged fragment of the feed molecule containing n-i carbon atoms (3). We will not consider or report the X_{ij} values here. They are available in the original sources (2–6). They refer to chain-propagating processes whose probabilities are difficult to interpret since they involve surface population densities of carbenium ion species.

TABLE 2

Protolysis Reactions of Hexanes

Reaction	RPP
$C_6H_{14} + SH \rightarrow C_6H_{13}S + H_2$	X_{00}
$C_6H_{14} + SH \rightarrow C_5H_{11}S + CH_4$	X_{01}
$C_6H_{14} + SH \rightarrow C_4H_9S + C_2H_6$	X_{02}
$C_6H_{14} + SH \rightarrow C_3H_7S + C_3H_8$	X_{03}
$C_6H_{14} + SH \rightarrow C_2H_5S + C_4H_{10}$	X_{04}

In order to make a quantitative estimate of all these probabilities, we have previously (3) provided a detailed description of the method for calculating the RPPs. This procedure disentangles the various paths that lead to the formation of a given product and yields the RPPs which quantify the processes by which the feed is converted. All such RPP values have now been calculated for n-hexane from data in (2), for 2-methylpentane (3), 3-methylpentane (4), 2,3-dimethylbutane (5), and 2,2-dimethylbutane (6), and only those referring to the protolysis reactions are shown in Table 3.

The rate expression for the protolysis of hexanes has also been developed in previous work (7) and is as follows:

$$\frac{dX}{d\tau} = \frac{A_1 \frac{1 - X}{1 + \varepsilon X} + A_2 \left(\frac{1 - X}{1 + \varepsilon X}\right)^2}{1 + B\left(\frac{1 - X}{1 + \varepsilon X}\right)} [SH]_0 (1 + Gt)^{-N},$$

where X is the fractional conversion of the reactant, τ is the space time, t is the time on stream, $[SH]$ is the initial concentration of active sites, G and N are aging parameters, and A_1, A_2 and B are parameters of the rate expression given by:

$$A_1 = \frac{\frac{k_0 I_1}{I_0} + \Sigma\, \alpha_n \cdot I_n \cdot {}_nK_n [C_6H_{14}]_0}{1 + (\Sigma\, \alpha_n \cdot {}_nK_n + \Sigma\, \alpha_n \cdot {}_nN_n K_{nn})[C_6H_{14}]_0}$$

TABLE 3

RPP Values for The Protolysis of Hexanes over H–Y[a]

Protolysis RPP	n-C_6 (2) 500°C	2-MC_5 (3) 400°C	2-MC_5 (3) 500°C	3-MC_5 (4) 400°C	2,3-DMC_4 (5) 400°C	2,2-DMC_4 (6) 500°C
X_{00}	0.000	0.005	0.092	0.113	0.005	0.000
	(0%)	(2%)	(14%)	(35%)	(13%)	(0.0%)
X_{01}	0.000	0.014	0.017	0.057	0.021	0.319
	(0%)	(5%)	(3%)	(18%)	(55%)	(63%)
X_{02}	0.066	0.005	0.009	0.051	0.000	0.042
	(8%)	(2%)	(1%)	(16%)	(0%)	(8%)
X_{03}	0.631	0.148	0.418	0.000	0.012	0.000
	(76%)	(53%)	(62%)	(0%)	(32%)	(0%)
X_{04}	0.133	0.109	0.133	0.099	0.000	0.148
	(16%)	(38%)	(20%)	(31%)	(0%)	(29%)
Total	0.830	0.281	0.669	0.320	0.038	0.509

[a] The value in each cell is the probability that the feed molecule will be converted by that process. The values in brackets represent the percent of all *initiation* reactions proceeding by the given path.

$$A_2 = \frac{-\sum \alpha_n \cdot I_n \cdot {}_nK_n[C_6H_{14}]_0}{1 + (\sum \alpha_n \cdot {}_nK_n + \sum \alpha_n \cdot K_n \cdot K_{nn})[C_6H_{14}]_0}$$

$$B = \frac{[k_0/I_0 - \sum \alpha_{n \cdot n}K_n + \sum \alpha_n \cdot {}_nK_n \cdot K_{nn})][C_6H_{14}]_0}{1 + (\sum \alpha_n \cdot {}_nK_n + \sum \alpha_n \cdot {}_nK_n \cdot K_{nn})[C_6H_{14}]_0}$$

The IRRs are in turn defined as the initial rates or individual processes in the chain mechanism and are calculated (3) from

$$\mathrm{IRR}_i = \mathrm{RPP}_i * (A_1 + A_2)/(1 + B) = \mathrm{RPP}_i * r_0$$

where r_0 is the total rate of the initiation reactions.

The values of the IRRs thus obtained for the initial protolysis of all the hexanes are given in Table 4.

DISCUSSION

Reaction Path Probabilities (RPPs)

We begin by noting that the various results were obtained at 400°C, or at 500°C, or at both temperatures. From studies of 2-methylpentane, where both temperatures are available, we see that the increase in temperature causes the total of the RPPs for initiation to increase by a factor of two (see Table 3). This means that the total of the probabilities of chain propagation decreases. An increase in the total *probability* of protolysis indicates that protolysis is a process with a higher activation energy than chain propagation, as befits an initiation reaction in any chain process.

We can also see that the normal alkane (n-C_6) shows the greatest tendency to protolyse, i.e., the least tendency to propagate chains. As a consequence, it has the smallest contribution to conversion made by second-order chain propagation reactions. This agrees with the finding (2) that the kinetics of this, and of all other normal alkanes studied to date (8), are well represented by an expression lacking the second-order term required for the interpretation of the kinetics of most branched alkanes (7, 9). The reason for this low probability of propagation is most likely the absence of weak C–H bonds in this type of molecule.

In keeping with this idea, we note that 2,3-dimethylbutane cracks almost completely via the chain process. At 400°C only 4% of its conversion is due to protolysis. Out of this small contribution by protolysis, about 32% is due to the splitting of the central C–C bond and 14% to the protolysis of each of the four methyl groups. The protolysis of a hydrogen atom contributes 6% for each of the two tertiary atoms suspected of contributing to this reaction. Unlike in the case of n-C_6, here the second order term in the kinetic rate expression is necessary in order to fit the rate data and to account for the largely second-order rate of conversion.

When we examine the protolysis of hydrogens in various molecular species we note that protolysis of a hydride is a particularly difficult reaction. However, the data on 2-methylpentane show that, in this molecule, and probably in all others, this reaction increases rapidly with temperature, more rapidly than any of the other initiation reactions. We conclude, that hydride protolysis has the highest activation energy of all the protolysis processes, making it a difficult reaction at low temperatures and the most likely reaction when temperatures are high. The probability of this reaction also varies greatly with the

TABLE 4

Individual Reaction Rates (IRRs) for Hexane Protolysis (in $\mathrm{min}^{-1} * 10^{-3}$)

Molecular structure	r_{00} H_2	r_{01} CH_4	r_{02} C_2H_6	r_{03} C_3H_8	r_{04} C_4H_{10}	Protolysis rate	Overall rate	CL
C–C–C–C–C–C								
500°C (2)	0.000	0.000	0.986	9.43	1.99	12.4	14.9	1.2
C–C–C–C–C | C								
500°C (3)	119	21.9	11.7	539	172	863	1290	1.5
400°C (3)	0.135	0.377	0.135	3.99	2.93	7.57	26.9	3.5
C–C–C–C–C | C								
400°C (4)	1.92	0.963	0.862	0.000	1.67	5.41	16.9	3.1
C–C–C–C | | C C								
400°C (5)	0.341	1.43	0.000	0.820	0.000	2.60	68.2	26
C | C–C–C–C | C								
500°C (6)	0.000	0.182	0.024	0.000	0.084	0.290	0.568	2.0

type of hydrogen present in the molecule. In n-C_6 and 2,2-dimethylbutane, where only primary and secondary hydrogens are present, the protolysis of hydrogen is so slow as to be unnoticeable. It is noticeable but minor in 2-methylpentane and prominent in 3-methylpentane, indicating that bond strengths or frequency factors (or both) of tertiary hydrogens are significantly different in various molecules.

In general, the formation of C_3 ions is the most favoured initiation process, as evidenced by the major contribution of the 03 process in all cases where it is possible. The next most common process is 04, which leaves a C_2 carbenium ion on the surface. We note that the process which leaves C_4 ions on the surface (02) is less favoured than the complementary 04 process which leaves behind the smaller C_2 carbenium ion. This is clearly shown in the ratio 04/02. These two probabilities arise when the same bond is protolysed and the choice is whether the C_4 or the C_2 fragment remains on the surface. As we see in Table 3, this ratio varies from 2 for n-hexane and 3-methylpentane, to 20 for 2-methylpentane where it remains fairly constant with temperature. Why the C_2 ion is more stable on the surface than the larger C_4 ion is not clear. The difference in this ratio in the protolysis of various molecules must arise either from differences in the stearic configuration of the residual C_4 ion which is formed from the various molecules during protolysis, i.e., before surface rearrangement can take place, or from the configuration of the transition state itself. What is clear is that small ions may be more common on the surface than one might have supposed. However, processes which leave C_1 ions on the surface do not seem to take place at all.

Another perspective on the protolysis reaction is obtained by examining the normalised *internal probabilities* of the various initiations in the total probability for protolysis, i.e., the individual probabilities of protolysis divided by the sum of all probabilities for protolysis for that molecule. These numbers are shown in brackets in Table 3. In the simple case of n-hexane, we see that none of the "difficult" processes are present: only the cracking of the central bond, which accounts for 76% of all protolysis, and the much less-likely cracking of the β-bonds (02 + 04) which together account for the remaining 24%.

As soon as tertiary carbons appear, so do tertiary groups. As a consequence, both 00 and 01 processes become measurable. The relative contributions of these two processes depend on the temperature and the molecular configuration, with 00 gaining prominence at higher temperatures, at least in 2-methylpentane cracking. In 2-methylpentane, in fact, all processes are possible and we see most clearly the prominence of the 03 as the dominant C–C bond cracking processes, followed by 04 with relatively small contributions from other paths. The 00 path is the exception; it is not a major path at 400°C but becomes a significant contributor at 500°C, where the high activation energy and simple stearic requirements of hydride abstraction allow this reaction to emerge as a significant contributor to chain initiation, even to the overall conversion.

In 3-methylpentane, where the 03 process is impossible, the 02 + 04 process becomes the dominant C–C scission, contributing 47% (i.e., 23.5% per β-bond) of the rate of initiation. At the same time, there is an increase in the reactivity of the tertiary hydrogen, with the result that 00 becomes a dominant protolysis reaction, with the single tertiary hydrogen contributing 35% of the rate of initiation. The scission of the tertiary methyl group, augmented by any cracking of the other two α-bonded methyls, contributes 18% to the initiation. Since the reported data are for 400°C, one might expect that the production of protolytic hydrogen will be even more prominent at higher temperatures.

The 2,2-dimethylbutane molecule has only two bonds which are protolysed at 500°C: the α-bonds attaching the methyl groups, and the β-bond next to the teritary carbon. There are no tertiary hydrogens to facilitate chain propagation. As a result, the reaction is too slow to study coveniently at lower temperatures and even at 500°C the primary and secondary hydrogens are essentially inactive. Of the active bonds, the α-bonds are somewhat less active than the β-bond, given that there are four of them accounting for about 15% of the initiation each, as compared to about 30% due to the single β-bond. We want to point out here that the simple process of counting all α-bonds as equivalent in their contribution to X_{01} may be valid in 2,3-dimethylbutane but is probably inaccurate for 2,2-dimethylbutane and in molecules such as 3-methylpentane. It will take studies of isotopically-marked compounds to unravel the RRPs of the individual methyl groups in such cases. New possibilities are now open for isotopic mixing studies to supply further details on the mechanism of protolysis, using the experimental selectivities of products from isotopically marked reagents to yield this kind of detailed mechanistic interpretation.

Finally, we can consider why the 2,3-dimethylbutane molecule is so resistant to all forms of protolysis, as compared to conversion by chain processes. Some 96% of this molecule converts by chain propagating reactions, probably due to the ease, relative to alternative reactions, of transferring one of the two tertiary hydrogens to a carbenium ion. At the same time, the overall rate is fast in this molecule. We could say that this is a fairly "refractory" molecule, with a rate of protolytic cracking that is a factor of three smaller than that of 2-methylpentane at 400°C, and a factor of two smaller than 3-methylpentane. This behaviour seems to be related to the number of tertiary C–H bonds in a molecule. However, the overall rates of such isomers are enhanced by chain propagation, which is made possible by the presence of reactive tertiary hydrogens. This means that 2,3-dimethylbutane has a low rate of initiation and a high rate of propagation (two tertiary hydrogens are available). The resulting overall rate is high as a result of the vigorous rate of bimolecular reactions.

Individual Reaction Rates (*IRRs*)

The average activation energy of protolysis must be about 240 kJ/mol (~58 kcal/mol), since the overall rate of protolysis increases with temperature so that the IRRs at 500°C are higher than at 400°C by more than two orders of magnitude (see Table 4). Individual protolysis reactions show a range of activation energies ranging from 330 kJ/mol (~79 kcal/mole) for hydride abstraction to 210 kJ/mol (~51 kcal/mole) for the cracking off of a C_4 paraffin via the 01 and the 04 reaction. For some reason the alternative process of protolysing the β-bond 02, which leaves a C_4 ion on the surface, shows a higher activation energy (230 kJ/mol) than 04. The overall conversion has an activation energy of 205 kJ/mol (49 kcal/mol); significantly lower than the protolysis reactions taken as a group but only slightly less than protolysis via 01 and 04. More precise estimates of these activation energies are available in (3). With caution, we will take these trends and magnitudes to apply to the other C_6 molecules.

Surprisingly, the individual reaction rate of 03 with an activation energy of 250 kJ/mol shows a higher activation energy than all the other protolysis reactions, except of course 00. The high activation energies of 00 and 03, compared to 01, 02 or 04, indicate that the bonds next to the tertiary carbon are by turns weaker for hydrogen and stronger for C–C than corresponding bonds which are one carbon removed. Furthermore, the frequency factors for these scissors are higher than those for the other processes. Long-standing literature indicates that the C–C bond is somewhat stronger in *i*-butane than in *n*-butane (10), for example, so the fact that 02 has an activation energy of 230 kJ/mol while 03 has 250 kJ/mol might have been expected. Primary and secondary hydrogens seem to be so strongly bonded that they play no obvious role at our temperatures. The fact that 01 has a low activation energy suggests that it is the methyl group at the end of the linear portion of the molecule that is the most active. Otherwise one would expect 03 to have a lower activation energy than 01.

The availability of initial reaction rates for the various protolysis processes provides an opportunity to examine the "protolysability" of various corresponding moieties in the five C_6 isomers. For example, Table 4 shows that the protolysis of hydrogen is so slow as to be undetectable in *n*-hexane at 500°C and is barely noticeable in 2-methylbentane at 400°C. In 3-methylpentane it is some fifteen times faster than in 2-methylpentane at the same temperature. This is an unexpected difference, in view of the small difference in the environment of the tertiary hydrogen in 2-methylpentane and 3-methylpentane and must indicate a significant difference in the transition states of the two reactions. The factor of two thousand which differentiates hydride protolysis at the two temperatures in 2-methylpentane gives us a clue. Such a change in rate requires a very high activation energy.

In view of this, the fact that hydrogen is produced by protolysis at observable rates must be the result of an entropy of activation which leads to a high frequency factor. At this time we do not know whether the difference in hydride reactivity between 2- and 3-methylpentane is due to a difference in activation energies, or in frequency factors, or both. There are indications from other work that a compensation effect is operating in hydrocarbon cracking; i.e., the free energy of activation is staying relatively constant while both activation energy and frequency factors vary in the same direction (11).

Table 4 shows that rates differing by some five orders of magnitude can be measured using our techniques. This is a sufficient range to allow us to observe vastly disparate reaction rates in the isomers of a simple paraffin molecule. Such disparate rates are clearly the cause of the "refractoriness" effect observed in the cracking of the complex mixtures of hydrocarbons (12) which constitute commercial gas oils.

Reaction Chain Length

Another view of the overall cracking process is obtained by considering the chain length in the various reactions. Chain length is defined as the rate of the overall reaction divided by the rate of initiation; or alternatively, as the reciprocal of the total probability of initiation. They are reported in Table 4 under CL, where they are seen to be low for *n*-hexane and 2,2-dimethylbutane, the two molecules without tertiary hydrogens. In the molecules containing tertiary hydrogens, chain lengths are high and vary from 3.2 for 3-methylpentane to 26 for 2,3 dimethylbutane. We note once more that chain processes produce no olefins; therefore, the longer the chain length, the larger will be the paraffin-to-olefin ratio in the products.

Temperature effects are illustrated by 2-methylpentane, where the chain length decreases from 3.5 to 1.5 as temperature rises from 400 to 500°C; this illustrates the increasingly monomolecular nature of the overall conversion as temperature is increased. The effect indicates that, as temperature is increased, the paraffin-to-olefin ratio will decrease as well. A shorter chain length means less isotopic mixing and smaller average product molecular weight, also in keeping with established facts.

The Addition of Olefins

Table 4 brings out an interesting sidelight, one which comes from consideration of the contribution of chain processes to the overall rate of cracking. If the rate of initiation in a given molecule is zero, the overall rate of conversion for that molecule as a pure feed will be zero, no matter how facile the chain processes may be for that molecule. This kind of thinking led to earlier suggestions that olefins are essential to initiate the cracking of paraffins (13–15), since paraffins themselves cannot form carbenium ions directly.

Although we now believe that paraffins self-initiate by forming carbonium ions on strong Brønsted sites, which then form carbenium ions by protolysis, the issue of enhancing the reaction rate by additives is not dead. It seems reasonable to expect that a molecule such as *n*-hexane, which cracks mostly by protolysis, will not benefit from the addition of carbenium-ion-forming species, as the additional conversion to be expected from such foreign-carbenium-ion-catalysed chain processes is small. On the other hand, a molecule that cracks mostly via a chain process and has trouble providing carbenium ions by protolysis (perhaps 2,3-dimethylbutane is such a molecule) may well crack at a lower temperature if the slow formation of carbenium ions by protolysis is replaced by an easier and faster carbenium-ion-forming raction due to the adsorption of an olefin on the Brønsted sites of the catalyst.

In the many papers which have examined the effects of added olefins in speeding up the cracking reaction, there is much contradictory evidence as to the efficacy of this procedure (13–19). The confusion is no doubt partly due to this difference in the dependence of various molecules on chain propagation as a means of conversion. This is further confounded by the fact that these effects are quite temperature dependent, and perhaps dependent on catalyst formulation as well. One might imagine a molecule which can not be protolysed but has extractable hydrogens and therefore does not react by itself. Such a molecule may be made to react in the presence of olefins.

Test Reactions

The cracking of certain hydrocarbons, e.g., some of the C_6 paraffins, has been used to evaluate catalyst performance (20–31). Such reactions offer a number, calculated from easy-to-obtain experimental data generated using simple test reactors, which is in some way related to the effectiveness of the catalyst. With this in mind, the "alpha test'' and the ''constraint index'' were devised to offer guidance as to the activity and diffusion properties of new cracking catalyst formulations. It is not surprising that when these procedures were introduced, their proponents did not fully appreciate how very complex and different is the behaviour of various hydrocarbons on any one catalyst, let alone what mechanistic complexities may transpire when different catalysts are used to crack the same molecule at different temperatures. These tests may still supply useful information, but we now know that their interpretation is not as simple as was initially supposed.

Very little can be said at this time about the meaning of the alpha test or the values reported as the constraint index. In view of the observed shift from chain processes to simple protolysis which takes place with increased temperature, and the consequent fact that at low temperatures branched C_6 molecules crack predominantly by chain processes while at higher temperatures they do not, it will be necessary to reinvestigate the mechanisms of the pertinent test reactions on the specific catalysts used in the earlier studies, and at the same experimental conditions, in order to understand the import of such values in the papers and patents which use them as a basis for further discussion.

It is also likely that the mechanism of reaction in all test molecules varies from catalyst to catalyst. There is good evidence, for example, that this is so for isobutane (32). If it is indeed so in general, and in these two test reactions in particular, we well may find ourselves without a simple reaction which can be used to evaluate either catalyst activity or diffusional ''constraint.''

The Future of Test Reactions

Although the role of the above considerations in guiding future research is not yet clear, what is clear is that traditional quasi-empirical studies of catalytic cracking are no longer satisfactory or appropriate for the advancement of understanding in this field. One can now calculate elementary kinetic parameters such as the reaction path probabilities (RPPs) and thereby allow for a better understanding of the quantum chemistry and stearic effects involved in the elementary processes of cracking. For example, the insights gained using our theoretical interpretation of selectivity data should make it possible to connect fundamental measures of catalyst behaviour such as the RPPs or the IRRs to the detailed measurements of solid state and surface properties, properties which we believe to be responsible for these gross phenomena. This improvement in understanding will compensate for the loss of the simple test reactions; help to improve commercial cracking catalyst formulations; and guide the selection of commercial reactor operating conditions.

In view of the above discussion, we believe that there are presently only three measures which provide unambiguous characterisation of the activity of a catalyst in a given system:

(1) the fraction of *initial* reaction proceeding via protolysis;

(2) the rate of the total *initial* reaction;

(3) the value of the decay rate constant (and decay exponent, if it is found to be other than one).

Initial reaction is defined here as the total initial rate of conversion measured (or, more accurately, calculated) at zero conversion. As for an alternative to the constraint index, at the moment there is none that we can propose.

CONCLUSIONS

We find that a wide range of different conversion processes takes part in the cracking of each of the various isomeric C_6 paraffins. The overall cracking processes of the individual isomers are characterised by large differences in the contributions of the various elementary reactions involved due to different specific rates and activation energies. One consequence of these major differences is that some isomers crack readily while others are quite refractory. As a further consequence of this, some molecules are converted mainly by chain reactions which involve bimolecular Rideal-type interactions with surface carbenium ions. At lower temperatures these molecules produce significant yields of isomers and relatively small amounts of olefins (high paraffin/olefin ratios) and small yields of the ''cracked'' (small) products.

Long-established methods of catalyst evaluation, such as the alpha test and the Constraint Index, are therefore an oversimplification of the many events which take place in cracking reactions. Such a ''black-box'' approach to the intricacies of catalytic cracking can not help but distort our understanding of the root causes underlying the effects being investigated and thereby limit and confuse our understanding of the real nature of the phenomena being observed.

There is reason to believe that the rate of overall reaction of chain-propagation-prone molecules can be affected, under certain circumstances, by the addition of carbenium-ion-forming species such as olefins. This would suggest that, in mixtures of hydrocarbons, there is a possibility of synergistic interaction between carbenium ions formed from one component of the feed with gas phase molecules of an other component of the feed. While researchers have generally avoided tackling this topic in any quantitative detail, such interactions should not prove difficult to quantify kinetically, or to implement in practice. When this is done, it may be possible to identify additives that assist cracking reactions, for example by enhancing selectivity or by controlling the formation of undesirable products such as coke.

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