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NOTE

Comparison of the Kinetics and Mechanism of 3-Methylpentane and 2-Methylpentane Cracking on USHY

Experimental time-average conversions and selectivities for reactions of 3-methylpentane and 2-methylpentane have been measured on USHY at 400°C to provide additional confirmation of our proposal that initiation of the cracking of saturated compounds takes place via the protolysis of a feed molecule and is always followed by some degree of conversion via a bimolecular, carbenium-ion-induced chain process (1–8).

The kinetic model appropriate to these reactions has been proposed previously (5) and used to fit the new experimental data. Optimum values of the parameters A_1, A_2, B, and G are given in Table 1. From Table 1 it can be seen that the value of A_1, which is related to the sum of the rates of all initial reactions occurring via both monomolecular and chain processes (3, 5), is higher in 3-methylpentane than in 2-methylpentane conversion. In both cases the A_2 parameter, which is related to the initial rates of bimolecular processes alone (3, 5), is necessary to achieve a statistically satisfactory fit, indicating that the contribution of the chain mechanism is important in the conversion of both molecules.

Parameter B in our model reflects the reflative values of adsorption constants of the reactant and products (5). For both feed molecules its value approaches −1, indicating that there is strong competition for adsorption sites by the product species. The values representative of the ratio of reactant adsorption constant to the weighted average adsorption constant for product species ($K_A/\overline{K}_P$) have been calculated (3) and are listed in Table 1. The values of $K_A/\overline{K}_P$ for both molecules confirm that products are more strongly adsorbed on the pristine Brønsted sites than are the feed molecules. From Table 1 it can also be seen that the value of $K_A/\overline{K}_P$ for 3-methylpentane is larger than that for 2-methylpentane. Now, since the olefinic products of both reactions are very similar, we can expect $\overline{K}_P$ values to be similar for the two reactants. This implies that K_A for 3-methylpentane is greater than for 2-methylpentane. This in turn means that 3-methylpentane forms carbonium ions more readily, though this facility evidently does not lead to a higher rate of monomolecular processes, as we can see in Table 4 where the absolute rate of initiation is seen to be greater for 2-methylpentane.

The catalytic product distributions obtained in the cracking of 3-methylpentane and 2-methylpentane over USHY are presented in Table 2. Initial selectivities were obtained by interpolating optimum performance envelopes for the various products (9).

The initial products from 3-methylpentane cracking consisted mostly of propylene, propane, C_4–C_5 paraffins, and C_6-paraffin isomers. Other significant primary products include ethylene, ethane, methane, C_4-olefins, and hydrogen. Relatively small amounts of C_5–C_6 olefins and coke were also present. Of the primary products propylene was found to be the major product of cracking (~30%). The C_6-paraffin isomer products consisted mostly of 2-methylpentane. This is probably a result of the lower activation energy needed for the methyl transfer to form a 2-methylpentyl ion as compared to the rearrangement of the parent 3-methylpentyl ion to form an *n*-hexyl or a dimethylbutyl ion (10). Nonetheless, even this isomerisation is relatively difficult and the molecule tends to crack.

In contrast the primary products from the conversion of 2-methylpentane consisted largely of C_6 paraffins with smaller amounts of propane, propylene, and C_4–C_5 paraffins. Small amounts of H_2, methane, ethane, ethylene, C_4–C_6 olefins, and coke were also present. The C_6 isomeric products, in that case, consisted mostly of 3-methylpentane which in that case was also the major reaction product (~45%). It seems reasonable to suppose that this difference in product selectivities is due to the relative ease of formation and higher stability of the 3-methylpentyl ion as compared to other C_6 carbenium ions. The consequence of these differences is that 45% more cracking-fragment molecules are formed in the reaction of 3-methylpentane, as shown in Table 2.

The reaction modes used to describe 3-methylpentane and 2-methylpentane cracking are presented in Table 3. Examining the results presented in Table 2 more closely it can be seen that some product ratios, for example the ratio of C_4 paraffins to C_2 olefins, are not one for either of the feed molecules. A value close to unity would be expected if the source of all such species was simply the monomolecular cracking shown in reactions [1]–[5] in Table 3. This fact, as well as the appearance of primary C_5 paraffins, leads us to suggest that in addition to mono-

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TABLE 1

Kinetic Parameters for 3-Methylpentane and 2-Methylpentane Cracking on USHY at 400°C

Kinetic parameters	3-Methylpentane	2-Methylpentane
A_1 (min^{-1})	0.426	0.355
A_2 (min^{-1})	−0.058	−0.031
B	−0.932	−0.960
G (min^{-1})	0.312	0.251
N	1.0	1.0
$\frac{K_A}{\bar{K}_P}$[a]	0.126	0.051
$\frac{A_1 + A_2}{1 + B}$ (min^{-1})	5.412	8.100

[a] Calculated by the equation $K_A/\bar{K}_P = (B + 1)\Sigma\ \mathcal{F}_i$ (3).

[b] A measure of the initial rate of reaction (8).

molecular reactions, cracking of 3-methylpentane and 2-methylpentane over USHY proceeds via a set of bimolecular processes. This view is supported by the nonzero values of the kinetic parameter A_2, which accounts for bimolecular processes in our kinetic treatment of the same data (see Table 1).

TABLE 2

Initial Selectivities for Cracking Reactions of 3-Methylpentane and 2-Methylpentane over USHY at 400°C

	Type[a]		Weight Selectivity		Molar Selectivity[b]	
Product	3MP	2MP	3MP	2MP	3MP	2MP
Hydrogen	(1 + 2)S	1S	0.0031	0.0003	0.1333	0.0129
Methane	1S	1S	0.0107	0.0027	0.0575	0.0145
Ethane	1S	1S	0.0177	0.0017	0.0507	0.0049
Ethylene	1S	1S	0.0322	0.0059	0.0990	0.0181
Propane	1S	(1 + 2)S	0.1775	0.0920	0.3469	0.1801
Propene	1U	1U	0.3259	0.0972	0.6673	0.1990
Isobutane	(1 + 2)S	(1 + 2)S	0.0629	0.0560	0.0933	0.0830
n-Butane	(1 + 2)S	(1 + 2)S	0.0123	0.0198	0.0182	0.0294
C_4 Olefins	(1 + 2)S	1S	0.0230	0.0098	0.0354	0.0150
Isopentane	(1 + 2)S	(1 + 2)S	0.0339	0.0798	0.0405	0.0953
n-Pentane	(1 + 2)S	(1 + 2)S	0.0051	0.0063	0.0061	0.0075
C_5 Olefins	1S	1S	0.0135	0.0065	0.0165	0.0080
2,3 Dimethylbutane	1U	1S	0.0283	0.0896	0.0283	0.0896
2-Methylpentane	1U	—	0.2006	Feed	0.2006	Feed
3-Methylpentane	—	1S	Feed	0.4326	Feed	0.4326
n-Hexane	1S	1S	0.0278	0.0490	0.0278	0.0490
C_6 Olefins	(1 + 2)S	1U	0.0087	0.0400	0.0089	0.0410
Coke	(1 + 2)S	(1 + 2)S	0.0205	0.0080	0.0205	0.0080
C_7 Paraffins	2S	2S	—	—	—	—
C_7 Olefins	2S	2S	—	—	—	—
C_8 Olefins	2S	2S	—	—	—	—
C_7–C_{10} Aromatics	2S	2S	—	—	—	—
Total			1.0037	0.9972	1.8505	1.2879

[a] 1, primary; 2, secondary; S, stable; U, unstable.

[b] Initial molar selectivities were calculated by using the relationship: Molar Selectivity = Weight Selectivity × (Molecular Wt. of Feed/Molecular Wt. of Product).

TABLE 3

Reaction Mechanism and Reaction Pathway Probabilities of 2-Methylpentane and 3-Methylpentane Cracking over USHY at 400°C

			RPP Values	
Entry No.	Reaction	Pathway	3MP	2MP
1	$C_6H_{14} + H^+B^-$	$\xrightarrow{X_{00}} H_2 + C_6H_{13}^+B^-$	0.113	0.005
2		$\xrightarrow{X_{01}} CH_4 + C_5H_{11}^+B^-$	0.057	0.014
3		$\xrightarrow{X_{02}} C_2H_6 + C_4H_9^+B^-$	0.051	0.005
4		$\xrightarrow{X_{03}} C_3H_8 + C_3H_7^+B^-$	—	0.148
5		$\xrightarrow{X_{04}} C_4H_{10} + C_2H_5^+B^-$	0.099	0.109
	Total monomolecular	Initiation processes	0.320	0.281
6	$C_6H_{14} + C_2H_5^+B^-$	$\xrightarrow{X_{20}} C_2H_6 + C_6H_{13}^+B^-$	0.000	0.000
7		$\xrightarrow{X_{21}} C_3H_8 + C_5H_{11}^+B^-$	0.000	0.000
8		$\xrightarrow{X_{22}} C_4H_{10} + C_4H_9^+B^-$	0.000	0.003
9		$\xrightarrow{X_{23}} C_5H_{12} + C_3H_7^+B^-$	0.000	0.089
10	$C_6H_{14} + C_3H_7^+B^-$	$\xrightarrow{X_{30}} C_3H_8 + C_6H_{13}^+B^-$	0.347	0.031
11		$\xrightarrow{X_{31}} C_4H_{10} + C_5H_{11}^+B^-$	0.000	0.000
12		$\xrightarrow{X_{32}} C_5H_{12} + C_4H_9^+B^-$	0.000	0.007
13	$C_6H_{14} + C_4H_9^+B^-$	$\xrightarrow{X_{40}} C_4H_{10} + C_6H_{13}^+B^-$	0.012	0.000
14		$\xrightarrow{X_{41}} C_5H_{12} + C_5H_{11}^+B^-$	0.003	0.000
15	$C_6H_{14} + C_5H_{11}^+B^-$	$\xrightarrow{X_{50}} C_5H_{12} + C_6H_{13}^+B^-$	0.044	0.006
16	C_6H_{14} + iso-$C_6H_{13}^+B^-$	$\xrightarrow{X_{60}}$ ios-$C_6H_{14} + C_6H_{13}^+B^-$	0.257	0.571
	Total bimolecular	Chain proceses	0.663	0.707
17	C_6H_{14}	$\xrightarrow{X_{kc}}$ Coke	0.017	0.012
18	$C_6H_{13}^+B^-$	$\xrightarrow{X_{b63}} C_3H_6 + C_3H_7^+B^-$	0.507	0.000

We propose that the carbenium ions left on the surface from initiation processes 1–5 can either desorb as olefins or participate in bimolecular reactions, i.e., chain reactions, by abstracting a hydride ion or some other moiety from a feed molecule. A set of possible hydride transfer and disproportionation reactions for 3-methylpentane and 2-methylpentane is presented in Eqs. [6]–[16] in Table 3. Hydride abstraction by $C_6H_{13}^+$ species which have undergone various methyl shifts leads to the formation of isomeric products from 3-methylpentane and 2-methylpentane, as shown in Eq. [16].

The chain termination step involves the return of a proton to the Brønsted base on the inorganic framework by an attached carbenium ion and the desorption of the remainder of the surface species as an olefin. Prior to this event a suitable carbenium ion, such as a $C_6H_{13}^+$, may also undergo β-scission to form propylene and a propyl ion, as indicated in Eq. [18]. Finally, one other reaction mode must be taken into account: the formation of coke, which can be written as shown in Eq. [17].

The reaction pathway probabilities were calculated using Eqs. [1]–[18] in Table 3 and the experimental molar selectivities of the initial products (8). The resultant reaction path probabilities (RPPs) are presented in Table 3. The individual reaction rates (IRRs) shown in Table 4 are calculated by multiplying the appropriate RPPs listed in Table 3 by the total rate of the reaction at initial steady state conditions. This rate in turn is calculated using the parameters listed in Table 1 (3, 8).

Entries [1]–[5] in Table 3 show that the probability of monomolecular processes is in total higher in 3-methylpentane than in 2-methylpentane reactions. Specifically the protolytic production of hydrogen shows a higher RPP in 3-methylpentane than 2-methylpentane conversion, which suggests that either the C–H tertiary bond in a 3-methylpentane molecule is weaker than in 2-methylpentane or that the other protolysis modes are more difficult. Examination of the absolute rates of hydrogen formation by protolysis as reported in Table 4 resolves the issue and confirms that this form of protolysis is indeed faster in 3-methylpentane. This conclusion is in agreement with the calculated activation energies for hydride abstraction from alkanes performed by Abbot and Head (11). These authors report that the activation energy for hydride abstraction leading to the formation of molecular hydrogen from 2-methylpentane is higher by about 17 kJ/mol than that from 3-methylpentane.

Further analysis of Table 3 reveals that cracking via disproportionation and hydride abstraction from the feed molecule is important in both cases, although there are some differences in the preferred reaction modes. For example, hydride abstraction from the feed molecule by $C_3H_7^+$ ions is the dominant process in 3-methylpentane conversion but is less active in 2-methylpentane reactions. This is no doubt due to the fact that the population of propyl ions is much smaller when 2-methylpentane is reacting, as evidenced by the low yield of C_3 species in general and of propylene in particular in that reaction. On the other hand, hydride abstraction by $C_6H_{13}^+$ species that have undergone rearrangement is more important in 2-methylpentane than in 3-methylpentane reactions. This reaction accounts for about 60% of the 2-methylpentane and only some 25% of total 3-methylpentane conversion. This time the reason is the relatively large population of 3-methylpentyl carbenium ions present in 2-methylpentane cracking, as evidenced by their dominance of the products. These ions do not seem to crack at all under our conditions. Disproportionation via a hydride transfer involving $C_3H_7^+$ to $C_5H_{11}^+$ species and a feed molecule is also more important in 3-methylpentane than in 2-methylpentane.

TABLE 4

Individual Reaction Rates for 3-Methylpentane and 2-Methylpentane Cracking on USHY at 400°C

		Reaction rate (min^{-1})	
Entry No.	IRR	3-Methylpentane	2-Methylpentane
1	r_{00}	0.611	0.041
2	r_{01}	0.308	0.113
3	r_{02}	0.275	0.041
4	r_{03}	—	1.198
5	r_{04}	0.536	0.883
6	r_{22}	—	0.025
7	r_{23}	—	0.721
8	r_{30}	1.878	0.251
9	r_{32}	—	0.057
10	r_{40}	0.065	—
11	r_{41}	0.016	—
12	r_{50}	0.238	0.048
13	r_{60}	1.391	4.625
14	r_{kc}	0.094	0.097
	Total	5.412	8.100

The chain propagation RPPs are clearly the result of both ionic strength effects and the effects of surface concentrations of the ionic species involved in the reaction. Both contribute to the absolute values of the RPPs. Interpretations based on ion concentrations alone can be used in this case are because the catalyst, and hence the sites, are the same in both our studies. The interpretation of any RPP behaviour is further complicated by the fact that RPPs are probabilities of reaction, not absolute reaction rates.

The IRRs, on the other hand, provide an absolute measure of reaction rate. This method however requires that one obtain enough data to evaluate the rate parameters and hence the initial rate of reaction. By considering the sum of the IRRs of all the initiation reactions we see that the total rate of protolysis of 3-methylpentane is slower than that of 2-methylpentane. This agrees with the conclusion previously reached on the basis of kinetic parameters. The total rate of all the chain propagating reactions is also higher in 2-methylpentane conversion. It seems therefore that 3-methylpentane is a less reactive molecule which cracks rather than undergoing disproportionation or isomerising. It is also a molecule which causes more-rapid catalyst decay, presumably because it does not displace surface carbenium ions as readily by means of the chain propagating transfers of hydrogen atoms or other moieties.

Other processes, like coke formation, take place with relatively small probabilities for both of these molecules. In keeping with the higher rate of decay in 3-methylpentane cracking (see the values of *G*, Table 1) initial coke selectivity is higher for this molecule. Since we interpret coke formation to be the result of reaction between adjacent carbenium ions, this confirms the conclusion that 3-methylpentane cracking involves a less efficient process for displacing, and hence rotating, the population of such ions.

The classical β-cracking is apparently inactive for the 2-methylpentyl molecule, but active for the 3-methylpentyl molecule under our conditions. This surprising result tells us that the 2-methylpentyl ions prefer to isomerize to 3-methylpentyl ions which desorb rather than cracking by a classical β-scission. The 3-methylpentane on the other hand produces a much higher population of 3-methylpentyl ions, which in order to produce identifiable products must desorb directly as 3-methylpentenes or isomerize to other C_6^+ species. The methyl shift on the C_6^+ apparently requires activation to an energy level which is high enough for β-cracking. Desorption of isomerised C_6^+ species as olefins is apparently not a favoured reaction and the ion cracks rather than isomerising.

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