

Hydrogen Transfer Reactions in the Catalytic Cracking of Paraffins

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A study of the reactions of *n*-octane and *n*-dodecane on HY zeolite has shown that molecular hydrogen is not formed as an initial product of catalytic cracking of *n*-paraffins on this zeolite. Hydrogen gas was not detected as a product at any level of conversion up to 25% at 400°C. The observation of hydrogen as an initial product by other workers may be related to the presence of a hydrogen at a tertiary carbon in the reactant molecules used in such studies. Initial molar ratios of paraffin/olefin in the cracking products were found to be other than unity, confirming previous reports. However, consideration of the selectivities of all primary products formed, including the aromatics and coke, shows that the overall hydrogen balance closes without stoichiometric anomalies or the requirement that hydrogen ions associated with the active sites of the catalyst are consumed irreversibly. © 1987 Academic Press, Inc.

INTRODUCTION

For many years, interest has focused on the mechanism by which the cracking of paraffins is initiated on zeolite catalysts (1-6). One mechanism has been proposed (4) partly as a result of the reported formation of molecular hydrogen as an initial product, although it is not clear whether hydrogen formation was observed directly or indirectly (7). In other studies (5, 6, 8) apparently high levels of the ratio of paraffins/olefins initially formed in cracking *n*-heptane on zeolites led to the proposal that a dual mechanism is involved, in which both carbonium and carbenium ions are initially formed. This scheme incorporates a chain mechanism in which initiation can occur through hydrogen transfer reactions to existing carbenium ions on the surface from the feed paraffin. Other workers have suggested that high paraffin/olefin ratios found in paraffin cracking can be accounted for by an irreversible loss of hydrogen from the active sites of the catalyst itself (9).

In previous work (10) we have reported on the cracking of a paraffin mixture, consisting mainly of *n*-paraffins in the range C₆-C₂₄ on HY and on HZSM-5 at 400°C.

There we found no evidence for the formation of molecular hydrogen. To explain our observations we postulated in that work that in the absence of the formation of coke and aromatics as primary products (as was the case on ZSM-5) one paraffin molecule is produced for each feed molecule cracked, with the remaining products consisting of olefins. We proposed that each paraffin feed molecule is cracked by the initial formation of a pentacoordinated carbonium ion which cracks to give one paraffin molecule and an adsorbed carbenium ion. This residual carbenium ion undergoes further cracking to yield only olefin fragments resulting in paraffin/olefin ratios of less than one.

In contradiction to this simple picture, recent work on the cracking of *n*-heptane on HY zeolite appears to show initial paraffin/olefin ratios which are significantly higher than unity, apparently in the absence of coke and aromatics as primary products (5, 6). If this were the case for this pure paraffin, our previous conclusions regarding paraffin mixtures need to be reexamined. We have therefore undertaken a careful study of two pure paraffin feedstocks, *n*-octane and *n*-dodecane, to establish

whether any molecular hydrogen is in fact produced, and to examine the initial paraffin/olefin ratios.

EXPERIMENTAL

The feedstocks, *n*-octane (99.60%) and *n*-dodecane (99.60%), were obtained from Aldrich and used without further purification. The impurities present (*n*-octane: 3-methylheptane, 0.40%; *n*-dodecane: C₁₂ isomers, 0.40%) were taken into account in calculating initial selectivities.

HY zeolite (97.3% exchanged) was prepared from NaY (Linde Co., lot No. 45912, SK40) by repeated exchange with 0.5 *N* ammonium nitrate solution. Catalysts with mesh size 50/70 were steamed for 24 h at 200°C before use. Previous investigations (11) have shown that reactions are not diffusion controlled at 400°C using this particle size. All experiments were carried out at 400°C at 1 atm pressure. Blank runs were performed under the same conditions to ensure that the glass used to dilute the catalyst was inert.

Figure 1 shows a schematic diagram of the apparatus, which consists of five major parts: reactant injection system, reactor, product collection system, regeneration system, and product analysis system.

The injection system is a syringe connected to both a reactant reservoir and the

reactor and driven by a variable-speed motor which controls the injection rate.

The Pyrex or quartz tubular reactor is approximately 2 cm i.d. × 50 cm in length. The upper three-quarters is packed with a suitable inert material which provides a heat reservoir and acts as the preheating section. The catalyst particles are mixed with clean Pyrex glass particles of similar size and fill the bottom quarter of the reactor. The reactor is enveloped by three heating elements which are independently controlled by signals from three thermocouples located at appropriate positions in the reactor.

The product collection system consists of a water-cooled condenser, a liquid separation pot, a cold finger, and gas burettes, to separate and collect the liquid and gas products.

The regeneration system includes a drierite tube, a cupric oxide furnace, and an ascarite tube for the absorption of CO₂ produced during regeneration.

The product analysis system contains two gas chromatographs, one each to analyze the liquid and gas products.

Before a reaction run, the reactor is purged for 30 min with N₂ gas flowing at 280 ml/min. During this time the dried liquid separation pot and the cold finger are weighed and installed, one immersed in an

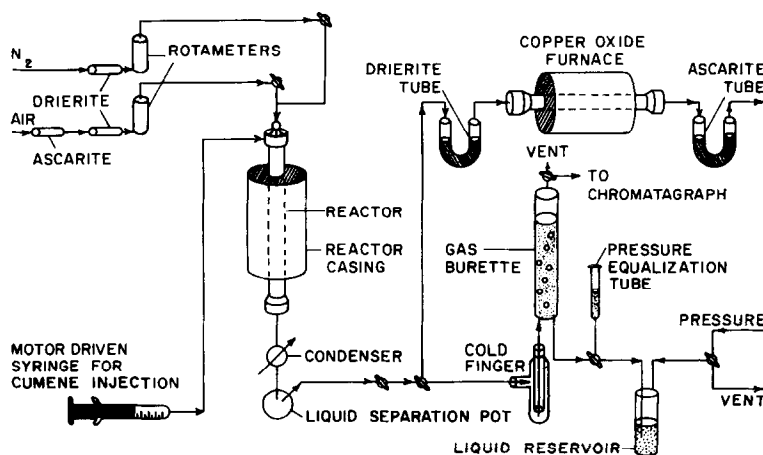


Fig. 1. Experimental apparatus used in cracking studies.

ice bath and the other in a dry-ice-acetone bath. The variable-speed motor is set to the desired speed and the gas burettes are filled with saline solution. Finally the injection nipple is connected to the top of the reactor.

Immediately after the prepurge period a defined amount of reactant is pumped through the reactor which contains a known weight of catalyst. The reactant is vaporized and heated up to the reaction temperature in the preheating section and converted in the catalyst bed; the reaction products flow to the condenser. The high-boiling products are condensed in the liquid separation plot and the cold finger, while the remaining gas products are collected in the gas burettes by the downward displacement of the saline production. As soon as the flow of reactant terminates, N_2 gas purges the reactor for a length of time, as preset by the operator, and the purge gases are collected in a gas burette. During this purge period, the liquid separation pot and the cold finger are warmed to room temperature in order to drive off dissolved gas in the liquid products. After the purge the weight of the remaining liquid products is determined.

Carbonaceous materials are deposited on the catalyst during this reaction and must be removed to restore the catalyst to its original activity for the next reaction run. To regenerate the catalyst, the reactor is heated to a standard temperature (500°C) and dry air, free of carbon dioxide, flows through it at a flow rate of 250 ml/min for at least 4 h, oxidizing carbonaceous materials into water vapor, carbon monoxide, and carbon dioxide. These regeneration gases pass first through a drierite tube to absorb water vapor and then into a cupric oxide furnace controlled at 350°C . In the furnace, carbon monoxide is converted into carbon dioxide and this, together with the rest of the carbon dioxide, is subsequently trapped in an ascarite tube at the exit of the furnace. In this way the weights of hydrogen and carbon in the coke can be determined.

Liquid products were analyzed by a Varian 600 gas chromatograph with a 60-m SE54 capillary column, and flame ionization detection. Products up to C_7 were eluted at 35°C , followed by a temperature program of $5^\circ\text{C}/\text{min}$ up to 300°C . Gaseous products were analyzed by a Carle SX1156 gas chromatograph. This enabled determination of all hydrocarbons in the range C_1 – C_5 and also direct determination of hydrogen if present. The identification of products was facilitated by use of a Finigan 1020 automated GC/MS.

A mass balance is performed for each reaction run to ensure that no leaks are present in the system and all products are accounted for. In each run the weight of the unconverted reactant and of each product made over the time $t = 0 \rightarrow t_f$ is determined. These results produce one data point on the plot of product yield versus cumulative conversion on each selectivity plot. Additional data points are obtained at constant catalyst-to-reactant ratio by changing the feed rate of the reactant but keeping the weight of feed delivered constant. Experiments carried out at various catalyst-to-reactant ratios, by changing the weight of catalyst in the reactor, allow a series of yield versus conversion loops to be drawn. These loops can be enveloped by a single curve known as the optimum performance envelope (12). We have found that these envelopes are in many cases indistinguishable from simple yield-conversion curves when studying single-component feedstocks (i.e., the loops are very flat). However, the distinction becomes very apparent when mixtures are used (13).

RESULTS AND DISCUSSION

Hydrogen Transfer

Initial selectivities for all primary products from the reaction of *n*-octane and *n*-dodecane on HY at 400°C are given in Tables 1 and 2, respectively. These were determined from the optimum performance envelopes (12) of each product by calculat-

TABLE 1

Product Types and Initial Weight Selectivities for Reaction of *n*-Octane on HY

Product	Type ^a	Initial selectivity
Ethane	2S	—
Ethylene	2S	—
Propane	(1 + 2)S	0.0500
Propylene	1U	0.1045
<i>n</i> -Butane	(1 + 2)S	0.1125
Isobutane	(1 + 2)S	0.1952
<i>trans</i> -2-Butene	1U	0.0593
<i>cis</i> -2-Butene	1U	0.0409
Isobutene	1U	0.1178
<i>n</i> -Pentane	1S	0.0281
2-Methylbutane	(1 + 2)S	0.1431
<i>trans</i> -2-Pentene	1U	0.0124
<i>cis</i> -2-Pentene	1U	0.0063
3-methyl-1-Butene	1U	0.0022
2-methyl-1-Butene	1U	0.0210
2-methyl-2-Butene	1U	0.0482
1-Pentene	1U	0.0032
<i>n</i> -Hexane	2S	—
2-Methylpentane	2S	—
3-Methylpentane	2S	—
2,3-Dimethylbutane	2S	—
2-Methylhexane	2S	—
3-Methylhexane	2S	—
2,3-Dimethylpentane	2S	—
2-Methylheptane	1S	0.0250
3-Methylheptane	1S	0.0110
4-Methylheptane	2S	—
2,3-Dimethylhexane	2S	—
2,4-Dimethylhexane	2S	—
2,5-Dimethylhexane	2S	—
Toluene	2S	—
C ₈ aromatics	(1 + 2)S	0.0125
C ₉ aromatics	(1 + 2)S	0.0038
Coke	(1 + 2)S	0.0180
		1.014

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

ing the slope at the origin. Primary products are defined as those having envelopes with nonzero slope at the origin; secondary products have zero slope at the origin. This is illustrated in Figs. 2 and 3 for some typical examples. In addition, from the shape of the optimum performance envelope, products can be classified as stable or unstable (12).

TABLE 2

Product Types and Initial Weight Selectivities for Reaction of *n*-Dodecane on HY

Product	Type ^a	Initial selectivity
Ethane	2S	—
Ethylene	2S	—
Propane	(1 + 2)S	0.0180
Propylene	1U	0.0753
<i>n</i> -Butane	(1 + 2)S	0.0321
Isobutane	(1 + 2)S	0.0753
<i>trans</i> -2-Butene	1U	0.0527
<i>cis</i> -2-Butene	1U	0.0316
Isobutene	1U	0.1205
<i>n</i> -Pentane	(1 + 2)S	0.0210
2-Methylbutane	(1 + 2)S	0.0853
<i>trans</i> -2-Pentene	1U	0.0231
<i>cis</i> -2-Pentene	1U	0.0141
3-methyl-1-Butene	2U	—
2-methyl-1-Butene	1U	0.0271
2-methyl-2-Butene	1U	0.0597
1-Pentene	1U	0.0073
<i>n</i> -Hexane	1U	0.0210
2-Methylpentane	(1 + 2)S	0.0452
3-Methylpentane	(1 + 2)S	0.0228
2,3-Dimethylbutane	2S	—
C ₆ olefins	1U	0.0916
<i>n</i> -Heptane	1S	0.0110
2-Methylhexane	(1 + 2)S	0.0251
3-Methylhexane	(1 + 2)S	0.0191
4-Methylhexane	(1 + 2)S	0.0073
2,4-Dimethylpentane	(1 + 2)S	0.0085
C ₇ olefins	1U	0.0339
Methylcyclohexane	T	—
Dimethylcyclopentanes	T	—
<i>n</i> -Octane	2S	—
2-Methylheptane	(1 + 2)S	0.0080
3-Methylheptane	(1 + 2)S	0.0091
4-Methylheptane	2S	—
2,3-Dimethylhexane	2S	—
2,4-Dimethylhexane	2S	—
2,5-Dimethylhexane	2S	—
Dimethylcyclohexanes	T	—
Trimethylcyclopentanes	T	—
Toluene	2S	—
C ₈ aromatics	2S	—
C ₉ aromatics	2S	—
C ₁₀ aromatics	2S	—
C ₁₀ + C ₁₁ paraffins	2S	—
C ₁₂ (skeletal isomerization)	1U	0.0361
Coke	(1 + 2)S	0.0169
		0.9987

^a 1, primary; 2, secondary; S, stable; U, unstable; T, trace amounts detected by GC/MS.

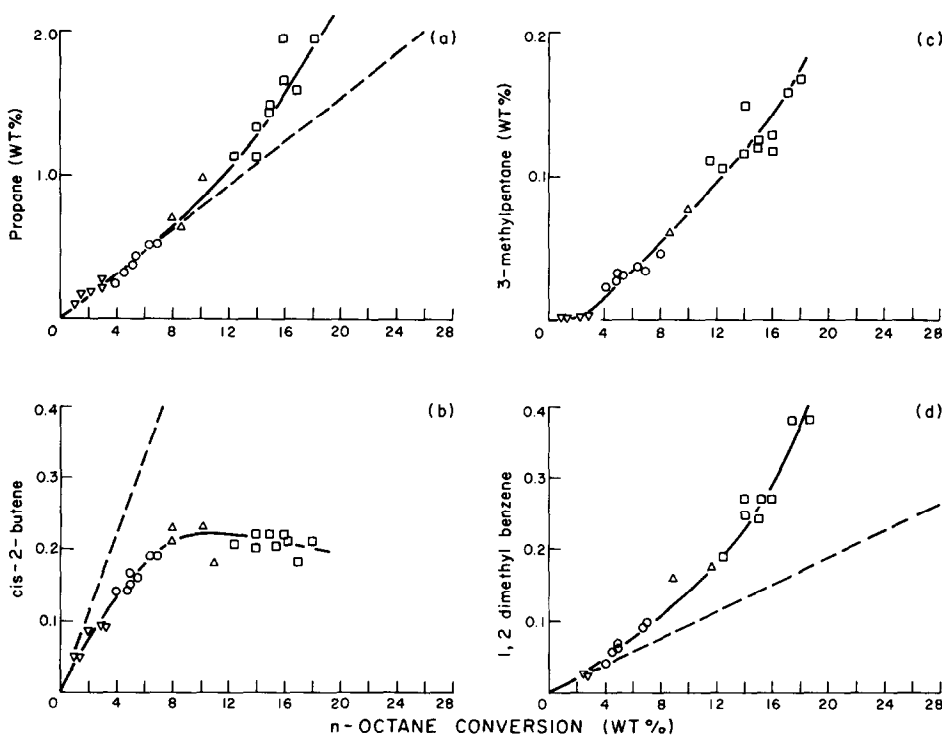


FIG. 2. Optimum performance envelopes for products of cracking *n*-octane on HY at 400°C. (a) Propane, (b) *cis*-2-butene, (c) 3-methylpentane, (d) 1,2-dimethylbenzene. Catalyst-to-reactant ratios: (▽) 0.0035, (⊙) 0.0345, (△) 0.069, (□) 0.276. Dashed lines show initial selectivity.

It should be noted that molecular hydrogen was not observed as a cracking product of either *n*-octane or *n*-dodecane at any level of conversion, nor have we observed this product in the cracking of *n*-hexadecane (11) on HY at the same temperature. This finding is in agreement with results for the cracking of *n*-heptane (5, 14) on HY zeolite in the temperature range 400–470°C. However, it has been reported that molecular hydrogen was observed (4) in other studies of paraffin cracking and reaction mechanisms were advanced partly on the basis of this finding. It appears that in many such studies direct measurement of hydrogen formation was not carried out, but that hydrogen yield was calculated on the basis of a shortfall in the mass balance (7). The suitability of this technique would appear suspect, unless coupled with a very accurate mass balance for all else. Our direct method of hydrogen determination enables

hydrogen detection down to levels of 0.001% (by volume) of the gas phase. This would correspond to less than 10^{-3} mol% of the feedstock cracked, which would certainly permit detection of the levels of molecular hydrogen reported by others.

Ongoing studies on catalytic cracking of a wide variety of hydrocarbons on HY zeolite support the idea that initial evolution of molecular hydrogen is associated with the presence of a hydrogen atom attached to a tertiary carbon atom in the molecule. Other workers have also suggested that the extent of hydrogen evolution during cracking of alkanes is related to the degree of branching in the reactant (15).

Table 3 gives initial selectivities (on a molar basis) for products, corresponding to each carbon number for both olefins and paraffins. It can be seen from these that the molar ratios of total paraffin/olefin (P/O) are not unity for cracking either *n*-octane or

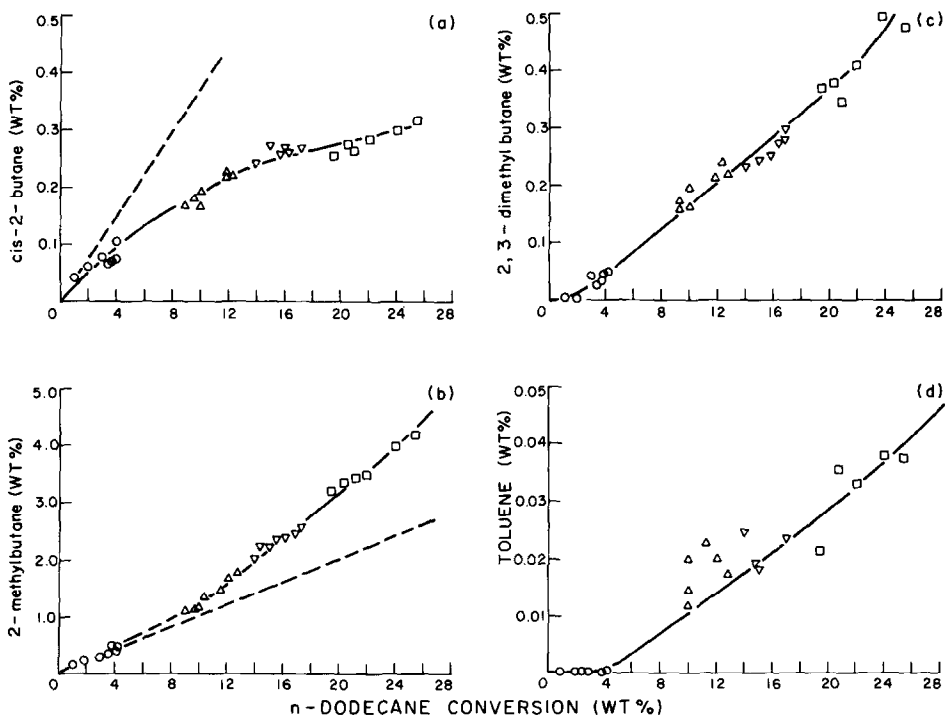


FIG. 3. Optimum performance envelopes for products of cracking *n*-dodecane on HY at 400°C. (a) *cis*-2-butene, (b) 2-methylbutane, (c) 2,3-dimethylbutane, (d) toluene. Catalyst-to-reactant ratios: (O) 0.0033, (Δ) 0.0333, (∇) 0.0655, (□) 0.1400. Dashed lines show initial selectivity.

n-dodecane ($P/O = 1.18$ for octane, $P/O = 0.67$ for dodecane). This is in agreement with the report that a P/O ratio which is not

equal to unity has been found for the cracking of *n*-heptane on HY zeolite in the temperature range 400–470°C (6, 14). Now we

TABLE 3
Initial Molar Selectivities for Reaction of *n*-Octane and *n*-Dodecane on HY

Product	Initial molar selectivity					
	<i>n</i> -Octane			<i>n</i> -Dodecane		
	Paraffin	Olefin	Total	Paraffin	Olefin	Total
C ₃	0.1295	0.2836	0.4138	0.0695	0.3047	0.3743
C ₄	0.6048	0.4438	1.0486	0.3148	0.6217	0.9365
C ₅	0.2711	0.1520	0.4231	0.2510	0.3189	0.5699
C ₆				0.1759	0.1853	0.3613
C ₇				0.1207	0.0588	0.1795
C ₈	0.0360		0.0360	0.0255		0.0255
C ₁₂				0.0361		0.0361
C ₈ aromatic			0.0134			
C ₉ aromatic			0.0036			
Coke			0.0180			0.0169
Total moles/mole converted	1.041	0.879	1.952	0.9935	1.489	2.500

can see that this ratio is dependent on molecular length. Important consequences follow from this observation.

Before attempting to draw any mechanistic conclusions it is necessary both to examine the cracking mode for each paraffin and to ensure that all primary products have been accounted for.

From the initial selectivities for *n*-octane cracking (Table 3) it is apparent that C₃, C₄, and C₅ are the only cracking fragments formed (with a very small amount of C₉ aromatics). Methane was not detected at any level of conversion, while ethane and ethylene were observed in trace amounts only as secondary products.

Moreover, the molar ratio C₃/C₅ is very close to unity (0.98). This suggests that *n*-octane cracks almost exclusively according to Eqs. [1] and [2] (Table 4) with the selectivities shown. Equation [3] represents skeletal isomerization to form 2-methylheptane and 3-methylheptane. Both C₈ and C₉ aromatic species were detected as primary products (Eq. [4]). As no C₇ fragments were initially produced, a simple dimerization-cracking process (16) cannot account for the appearance of C₉ species. Instead, we

TABLE 4
Initial Selectivities for Cracking Processes

	Selectivity	
<i>n</i> -Octane		
C ₈ → C ₄ + C ₄	0.5243	[1]
C ₈ → C ₃ + C ₅	0.4180	[2]
C ₈ → C ₈ (skeletal isomers)	0.0360	[3]
C ₈ → aromatics	0.0170	[4]
C ₈ → coke	0.0180	[5]
Total	1.0130	
<i>n</i> -Dodecane		
C ₁₂ → C ₆ + C ₆	0.1807	[6]
C ₁₂ → C ₇ + C ₅	0.1795	[7]
C ₁₂ → C ₈ + C ₄	0.0255	[8]
C ₁₂ → C ₅ + C ₃ + C ₄	0.3842	[9]
C ₁₂ → C ₄ + C ₄ + C ₄	0.202	[10]
C ₁₂ → C ₁₂ (skeletal isomerization)	0.0361	[11]
C ₁₂ → coke	0.0169	[12]
Total	1.025	

TABLE 5

Hydrogen Balance for Reaction of *n*-Octane on HY

Product	Initial molar selectivity	Double bond equivalents	Hydrogen ^a selectivity
Paraffins	1.041	0	1.041
Olefins	0.879	1	0.879
Aromatics	0.0170	4	0.0688
Coke (C ₈ H ₁₀)	0.0180	4	0.0720

^a A closed hydrogen balance requires that one double bond and one paraffin are formed in each cracking event in *n*-octane.

believe that the C₉ aromatics are formed by methyl transfer to a C₈ precursor from species which are collectively called "coke." This is the residual material remaining on the catalyst surface after purging with nitrogen. The C/H ratio of the coke initially formed in *n*-octane cracking (Eq. [5]) was found to be ~0.80 which corresponds to an average C₈ aromatic species (C₈H₁₀). This does not mean that the residual material consists of adsorbed C₈ aromatic species, as both saturated and highly unsaturated species may well be present. However, for the purpose of selectivity calculations the "average coke" may be regarded as having this composition.

Having established that the only significant modes of cracking of *n*-octane on HY produce two fragments, it is possible to consider an overall initial hydrogen balance, as shown in Table 5. This shows that, when all initial products are accounted for, the molar ratio of paraffins to the double bond equivalents in unsaturated initial products is close to unity (1.02).

The molar ratio

$$\left(\frac{\text{paraffins in product} - \text{paraffins in feed}}{\text{paraffins in feed}} \right)$$

is shown plotted against total conversion in Fig. 4. This function is a measure of total transfer hydrogen resulting in the production of coke, aromatics, and other species having a higher degree of unsaturation than monoolefins. The slope at the origin in Fig. 4 corresponds to an initial molar selectivity of 0.100. This agrees well with the hydro-

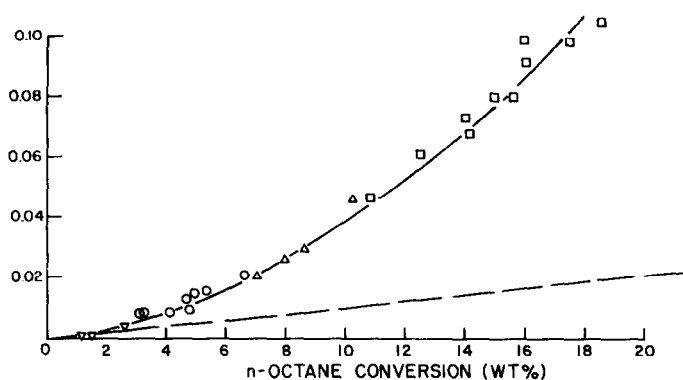


FIG. 4. Molar ratio of (paraffins in product-paraffins in feed)/(paraffins in feed) plotted against conversion for *n*-octane reaction. Dashed line shows initial selectivity. Symbols correspond to catalyst/reactant ratios in Fig. 1.

gen transfer required for the production of coke and aromatics from corresponding monoolefins (0.105) calculated as $3 \times$ (selectivity for aromatics and coke) C_8H_{10} composition for the coke and aromatics.

The same function is shown plotted for the cracking of *n*-dodecane in Fig. 5. This

shows that there is no initial hydrogen transfer. The slope at the origin is zero. Although Fig. 6 shows that coke is a primary product in dodecane cracking, the observed initial C/H ratio (~ 0.5) for this coke corresponds to the value for adsorbed paraffins. (Note, however, that the observed C/H ra-

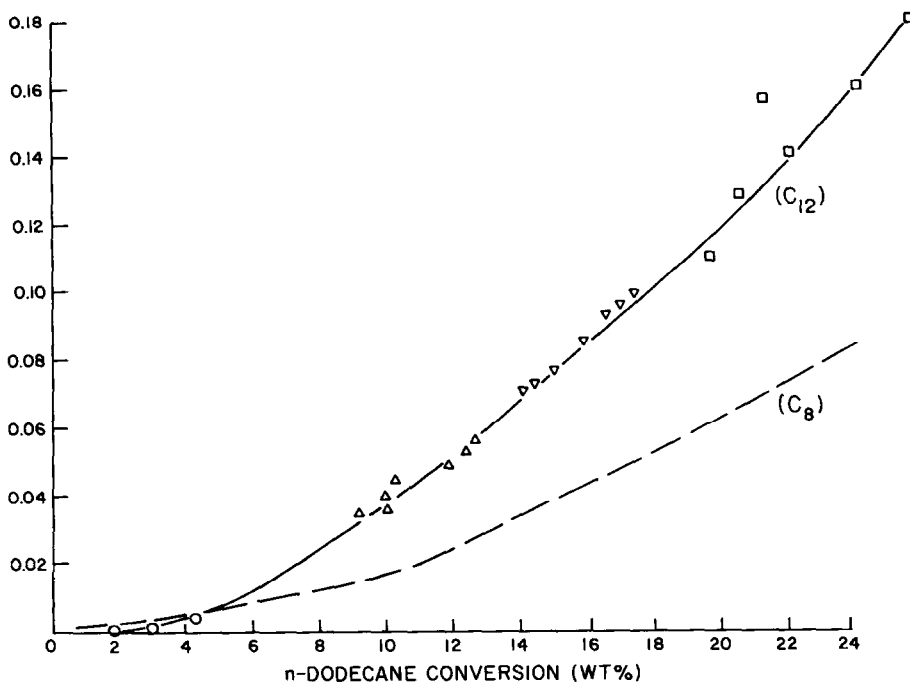


Fig. 5. Molar ratio of (paraffins in product-paraffins in feed)/(paraffins in feed) plotted against conversion for *n*-dodecane reaction on HY. The dashed line shows the corresponding function for *n*-octane compared on a molar basis. Symbols correspond to catalyst/reactant ratios in Fig. 2.

tio for coke increased to ~ 1.0 at conversion levels in excess of 20%.) This observation could well account for some discrepancies in reported paraffin/olefin ratios and in hydrogen balances. Unless a valid and careful extrapolation to initial conditions is carried out, greatly misleading conclusions can be drawn from data at conversions as low as 5%. In addition, the initial selectivity for aromatics formed from *n*-dodecane on HY is zero (Table 2), in agreement with the observed lack of initial hydrogen transfer (Fig. 5).

Figure 5 also shows the corresponding curve for hydrogen transfer for *n*-octane cracking, with the comparison being made on a molar basis. It is clear that although hydrogen transfer is more significant for cracking *n*-octane at very low conversions, the opposite is true at higher levels of conversion.

We have previously found (11) that the decay rate constant (k_{md}) and decay exponent (m) increase with the chain length of the paraffin molecule in the range C_8 – C_{16} . These results may be accounted for by a more rapid production of aromatics and highly unsaturated coke species from larger feed molecules, as reflected in the hydrogen transfer curves in Fig. 5. It is also apparent that while aromatic species can be formed from precursor C_8 , they are not formed directly from C_{12} .

The greater rate of hydrogen transfer associated with dodecane cracking at higher conversion may be associated with the formation of unsaturated cyclic species and coke from small olefins (C_3 – C_5) which in turn are formed in greater abundance from the longer-chain paraffins. It has been reported (7) in carbon-14 tracer experiments that coke appears to be formed mainly as a secondary product from small olefins (C_3 – C_5) during the cracking of *n*-hexadecane on silica–alumina at 372°C. Coke production from dodecane and cyclododecane has been found to be much lower than that from dodecene on rare earth-exchanged X zeolite. It was suggested that this is due to a

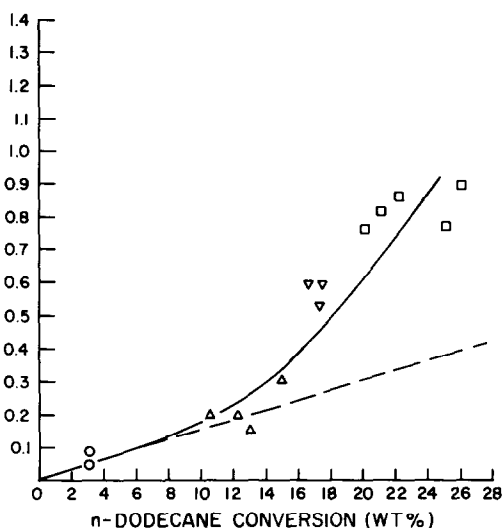


FIG. 6. Carbon in coke (wt%). Optimum performance envelope for coke formation from *n*-dodecane reaction on HY at 400°C. Symbols correspond to catalyst/reactant ratios in Fig. 2.

greater extent of condensation reactions of small olefins (18).

C_{12} Cracking Pattern

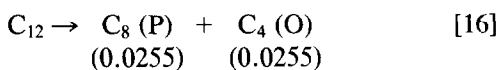
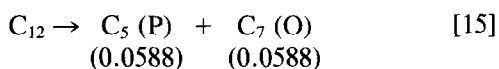
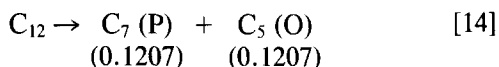
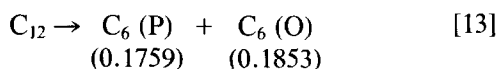
The initial molar selectivities for cracking products from *n*-dodecane are presented in Table 3. It is clear that a simple cracking mode giving two fragments cannot by itself explain the observed initial product distribution, as the molar ratios C_3/C_9 (∞), C_4/C_8 (36.7), and C_5/C_7 (3.2) are not equal to unity. The larger fragments (C_9 , C_8 , C_7) initially attached to the catalyst surface must undergo further cracking before desorption occurs, as previously shown in olefin cracking (19, 20). On this assumption we examine a simple cracking mechanism which can account for the observed initial product distribution, without invoking the more complex chain sequences proposed by others (5).

It can be seen that on the basis of the above reported zero initial hydrogen transfer and assuming sequential cracking of the attached fragment each *n*-dodecane molecule cracked will produce one molecule of product paraffin, and either one or two ole-

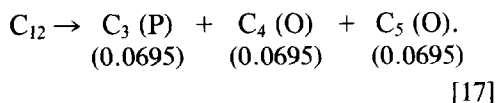
fin fragments. More than three fragments cannot be produced if it is taken that C_6 species initially formed do not undergo further cracking before desorption. This assumption will be justified later. It is also obvious that fragments smaller than C_3 cannot be cracked as methane, ethane, and ethylene are not initial products.

Equations [13]–[16] show the observed initial cracking modes leading to two fragments. (The designations (P) and (O) refer to paraffin and olefin, respectively.) The numbers in parentheses below each product indicate the observed initial selectivities (from Table 3). Selectivities for C_5 (O), C_5 (P), and C_4 (O) have been deduced from simple stoichiometry using the values of C_7 (P), C_7 (O), and C_8 (P), respectively, from Table 3.

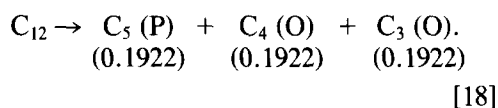
It should be noted that the ratio of observed initial selectivities for C_6 (P) and C_6 (O) is close to unity (0.95) which itself is suggestive of a simple cracking mode.



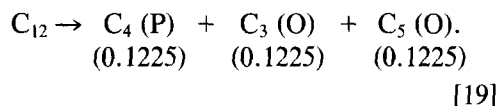
The selectivity for C_3 (P) in Eq. [17] can be assigned directly from Table 3 as this is the only cracking mode giving this product. Selectivities for C_4 (O) and C_5 (O) again follow from stoichiometry:



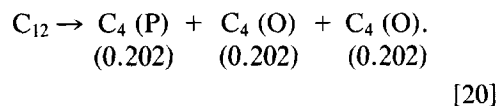
The selectivity for C_5 (P) in Eq. [18] is obtained by subtracting that for C_5 (P) in Eq. [15] from the overall value for C_5 (P) in Table 3:



Equation [19] must account for the remaining C_3 (O) initially observed:



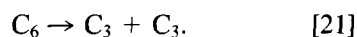
This leaves the cracking mode in which three C_4 fragments are formed:



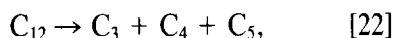
The selectivity for C_4 (P) in this process has been deduced by subtracting the C_4 (P) selectivity in Eq. [19] from the overall value in Table 3. Selectivities for C_4 (O) again follow from simple stoichiometry. Finally, the sum of the deduced selectivities for C_4 (O) in Eqs. [20], [18], [17], and [16] gives a value of 0.69, which agrees with the experimental value (0.62). Thus it would appear that the cracking processes for *n*-dodecane can be accounted for by postulating the fragmentation of feed molecules on active sites on the catalyst, without the necessity for a complex chain reaction scheme (5).

The suggestion that the cracking of a paraffin molecule can also be initiated by a hydrogen transfer from an existing carbenium ion (4, 5) cannot be rejected, but the observed product distributions do not require that this occurs, nor can the extent of this initiation process be deduced from the results presented here.

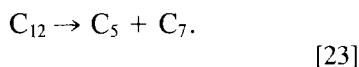
We assumed earlier that C_6 fragments do not undergo significant cracking before desorption. As no C_1 or C_2 initial products were detected, the only possible cracking mode is that given by Eq. [21] in which two C_3 species are formed:



We also know that C_3 and C_5 are both formed through the process



while C_5 can also be formed by the cracking mode



As the experimental molar ratio $C_3/(C_5-C_7)$ is close to unity (0.96) we conclude that the contribution from Eq. [21] is negligible.

Using the above we can see that the corrected selectivity value for olefin formation from *n*-dodecane lies between 0.977 and 1.01 (depending whether the experimental or deduced value for overall C_4 (O) is used). In either case the P/O ratio for *n*-dodecane cracking is close to unity (1.02–0.98). Initial selectivities for each cracking process are given in Table 4 for reaction of *n*-dodecane on HY. Table 6 gives corrected total initial selectivities for each C_n product for both *n*-octane and *n*-dodecane as per the consideration presented above.

The "Irreversible" Removal of Acid Hydrogens

It has been reported by several investigators that paraffin/olefin ratios greater than unity are observed for cracking single paraffins (C_n , $n < 8$) on zeolites (5, 6, 21). Release of hydroxyl hydrogens from the zeolite has been suggested (9) to account for

TABLE 6

Corrected Initial Selectivities for Cracking Products on HY

	<i>n</i> -Octane	<i>n</i> -Dodecane
C_3	0.2066	0.1281
C_4	0.5225	0.3199
C_5	0.2116	0.2178
C_6		0.1807
C_7		0.0898
C_8	0.0360	0.0128
C_{12}		0.0361
Aromatics	0.0170	
Coke	0.0180	0.0169
Total	1.011	1.002

TABLE 7

Restoration of Catalytic Activity for *n*-Hexadecane Cracking on HY by Regeneration in Air at 500°C

Run number ^a	Time-on-stream (s)	Conversion (%)
2	362	38.57
3	363	38.15
12	362	39.66
22	352	36.89
31	357	40.00

^a Intermediate run numbers were carried out at other times-on-stream.

those observations. Evidence for this is provided by the finding that catalytic activity for hexane cracking on HY zeolite could not be restored by calcination of the catalyst in air at 550°C (9, 23). Thus it was proposed that hydrogen is irreversibly lost from active sites present on the catalyst surface and this contributes to the formation of saturated cracking products. Our investigations on cracking of *n*-octane, *n*-dodecane, and *n*-hexadecane do not support this finding. Catalytic activity was fully restored by regenerating the HY in air over a 24-h period at 500°C. Table 7 shows that for a particular time-on-stream, catalytic activity for *n*-hexadecane cracking remains unchanged after more than 30 runs. We can only speculate as to the reason for the loss of activity observed by other investigators. For example, regeneration at too high a temperature will result in the loss of activity for paraffin cracking as Brønsted sites are converted into Lewis acid sites (21, 24). This could result from too rapid a regeneration and the consequent adiabatic heating of catalyst particles above the bulk temperature in the bed. Insufficient time of regeneration could also be a contributing factor.

CONCLUSION

No evidence for the formation of molecular hydrogen has been found for cracking of *n*-octane, *n*-dodecane, or *n*-hexadecane on HY at 400°C. This is in agreement with

studies of *n*-heptane cracking on HY in the temperature range 400–470°C.

We find that in *n*-octane cracking the experimental value for the initial paraffin/olefin ratio is unity provided all primary products including aromatics and coke are taken into account. This is also the case when the multiple fragmentation of the residual ion is considered in *n*-dodecane cracking. This conclusion is in conflict with recent studies on *n*-heptane cracking. However, we feel confident that our results must be correct because experimental technique involves a closed system in which both carbon and hydrogen balances of ~100% are routinely measured.

Paraffin/olefin ratios significantly in excess of unity for a simple paraffin feedstock such as *n*-heptane, where multiple fragmentation does not occur, and in the absence of other unsaturated initial products, i.e., coke and aromatics would appear to be an anomaly.

It seems that the initial paraffin/olefin ratio decreases with feed molecular chain length in a manner which indicates that after the initial cracking event the residual ion continues to crack into fragments between C₃ and C₆ in length, without desorption.

Our results are consistent with mechanisms of paraffin cracking involving formation of either carbenium ion or carbonium ion intermediates, and further study will be required to differentiate between these possibilities.

REFERENCES

- Greensfelder, B. S., Voge, H. H., and Good, G. M., *Ind. Eng. Chem.* **41**, 2573 (1949).
- Germain, J. E., "Catalytic Conversion of Hydrocarbons." Academic Press, New York, 1969.
- Pines, H., "The Chemistry of Catalytic Hydrocarbon Conversions." Academic Press, New York, 1981.
- Haag, W. O., and Dessau, R. M., "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. II, p. 305. Dechema, Frankfurt-am-Main, 1984.
- Corma, A., Planelles, J., Sanchez-Marin, J., and Tomas, F., *J. Catal.* **93**, 30 (1985).
- Corma, A., Fornes, V., Manton, J. B., and Orchilles, A. V., *Appl. Catal.* **12**, 105 (1984).
- Hightower, J. A., and Emmett, P. H., *J. Amer. Chem. Soc.* **87**, 939 (1965).
- Corma, A., Monton, J. B., and Orchilles, A. V., *Appl. Catal.* **16**, 59 (1985).
- Bolton, A. P., and Bojalski, R. L., *J. Catal.* **23**, 331 (1971).
- Abbot, J., and Wojciechowski, B. W., *Ind. Eng. Chem. PRD* **24**, 501 (1985).
- Abbot, J., and Wojciechowski, B. W., *J. Catal.* **104**, 80 (1987).
- Ko, A. N., and Wojciechowski, B. W., *Prog. React. Kinet.* **12**, 201 (1983).
- Pachovsky, R. A., John, T. M., and Wojciechowski, B. W., *AIChE. J.* **19**, 802 (1973).
- Corma, A., and Fornes, V., "Catalysis by Acids and Bases," p. 409. Elsevier, Amsterdam/New York, 1985.
- Planelles, J., Sanchez-Marin, J., Tomas, F., and Corma, A., *J. Mol. Catal.* **32**, 365 (1985).
- Bolton, A. P., and Bujalski, R. L., *J. Catal.* **18**, 1 (1970).
- John, T. M., and Wojciechowski, B. W., *Adv. Chem. Ser.* (1974).
- Nace, D. M., *Ind. Eng. Chem. PRD* **8**, 31 (1969).
- Abbot, J., and Wojciechowski, B. W., *Canad. J. Chem. Eng.* **63**(3), 451 (1985).
- Abbot, J., and Wojciechowski, B. W., *Canad. J. Chem. Eng.* **63**(2), 278 (1985).
- Benesi, H. A., *J. Catal.* **8**, 368 (1967).
- Ione, K. G., *Kinet. Catal.* **21**, 881 (1980).
- Tung, S. E., and McIninch, J., *J. Catal.* **10**, 175 (1968).
- Hopkins, P. D., *J. Catal.* **12**, 325 (1968).