Catalytic Cracking of *n*-Hexadecane

VI. Carbon-14 Tracer Studies of Secondary Reactions over Amorphous Silica-Alumina and Zeolite Catalysts

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The importance of some secondary reactions during the catalytic cracking of *n*-hexadecane over an amorphous silica-alumina catalyst and a zeolite-containing catalyst at 372°C were investigated using carbon-14 tracers. 1-Butene and 1-heptene tracers were used to determine the importance of the four butene isomers and 1-heptene as intermediates in secondary reactions over the amorphous silica-alumina. The butenes had a significant role in the formation of most products via secondary reactions, while 1-heptene was much less important. 1-Butene and toluene tracers were used to investigate their importance as intermediates in product formation over the zeolite catalyst. Although 1-butene was involved in the formation of a larger amount of the products than toluene, 1-butene was much less important as an intermediate over the zeolite catalyst than over the amorphous silica-alumina catalyst.

INTRODUCTION

The carbonium ion mechanism independently proposed by Greensfelder *et al.* (*1*) and by Thomas (*2*) is generally accepted for the catalytic cracking of hydrocarbons over solid acidic catalysts. The product distributions predicted by the cracking theory are substantially those found in practice for both amorphous and crystalline silica-alumina catalysts. Discrepancies have been attributed to thermal cracking, continually changing intermediate (*3*), a cyclic intermediate (*4*), and polymer breakdown (*5, 6*). Besides the primary cracking products formed from the hydrocarbon feed, there are also products produced by secondary reactions of the olefins and paraffins formed in the primary cracking reactions. These secondary reactions include isomerization, polymerization, alkylation, aromatization, and hydrogenation.

In previous papers in this series (*7–11*), secondary reactions in the catalytic cracking of *n*-hexadecane over amorphous and crystalline silica-alumina catalysts were examined using carbon-14 tracers to indicate the importance of certain compounds in secondary reactions. Van Hook and Emmett (*7–9*) and Hightower and Emmett (*10*) found that paraffins and ethylene took very little part in secondary reactions in the cracking of *n*-hexadecane over an amorphous silica-alumina catalyst at 372°C, while propylene and pentene appeared to contribute much more to the product distribution through secondary reactions. Hightower and Emmett (*10*) concluded that propylene and 1-pentene participated extensively in the formation of aromatics, but only a small fraction of the alkyl aromatics was formed by direct alkylation of benzene or toluene, with the exception of isopropylbenzene. Bordley and Emmett (*11*) extended the work to pure zeolite catalysts using propylene and toluene carbon-14 tracers. It was found that incorporation of radioactivity into the products was not as large over the zeo-

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lites as when amorphous silica-alumina catalysts were used.

n-Hexadecane cracks to form primary products, a, which then undergo secondary reactions to form products, i. The importance of a particular intermediate, a, in the secondary reactions is determined by adding a small amount of radioactive a to the n-hexadecane. In preceding studies, the contribution of an intermediate taking part in secondary reactions was measured by the $\alpha_a^i(\text{obs})$ value, where

$$\alpha_a^i(\text{obs})$$
$$= \left[\frac{\text{specific (molar) radioactivity of } i}{\text{specific (molar) radioactivity of } a}\right]$$
$$\text{(at reactor exit). (1)}$$

If all of product i were formed from a, the maximum α value, $\alpha_a^i(\text{max})$, would be obtained. The percent of i, denoted by P_a^i, produced by reactions involving a was given as

$$P_a^i = \frac{100}{n}\left[\frac{\alpha_a^i(\text{obs})}{\alpha_a^i(\text{max})}\right] \quad (2)$$

where n is the number of molecules of a reacting to form a molecule of i (10). Later (12), a more accurate expression for P_a^i was derived,

$$P_a^i = \frac{100}{n}\left\{\frac{\alpha_a^i(\text{obs})}{\alpha_a^i(\text{max})}[1 + S] - S\right\} \quad (3)$$

where S is the ratio of the product i formed from the added tracer to the product i formed from n-hexadecane.

$$S = \frac{Rg}{X_c N_i} \quad (4)$$

where R is the percentage of radioactivity in product i at the reactor exit, g is the molar ratio of tracer to n-hexadecane at the reactor entrance, X_c is the fractional conversion of n-hexadecane, and N_i is the number of moles of product i formed per 100 mol of n-hexadecane cracked. In almost all cases in this series of papers, S was so small that Eq. (2) was a satisfactory approximation. Estimates of $\alpha_a^i(\text{max})$ could be

made (13) for an integral reactor by making assumptions of reaction orders, etc. Van Hook and Emmett (7) estimated $\alpha_a^i(\text{max})$ to be between 1 and 2. Hightower and Emmett (10) estimated that $\alpha_a^i(\text{max})$ could be as high as 3. In these earlier papers, however, $\alpha_a^i(\text{obs})$ was used rather than P_a^i as an indication of the importance of an intermediate in secondary reactions because of the uncertainty in $\alpha_a^i(\text{max})$.

In the present study reaction kinetics are assumed which allow the calculation of the percentage of specific products formed from a specific intermediate without using α values. Carbon-14 tracers are used to determine the importance of the butenes and 1-heptene as intermediates in secondary reactions over an amorphous silica-alumina catalyst and 1-butene and toluene as intermediates over a zeolite catalyst.

METHODS

Experimental. The reactor system and experimental procedure have been described previously in detail (10, 12). The experimental conditions for each run are given in Table 1. Briefly, n-hexadecane vapor and a small amount of carbon-14 radioactive tracer were mixed with helium carrier gas and passed at a total flow rate of about 160 ml/min over 23.3 g of catalyst in a fixed bed reactor at 372°C. The total run time was 25 min. The products were collected and analyzed by gas chromatography, except the coke which was determined by combustion. The products were mixed with oxygen as they left the GC and burned to CO_2. The radioactivity of the CO_2 was determined with a Baird Atomic Co. VPC-164 geiger counter. The product distributions were determined in experiments without any tracer.

The amorphous silica-alumina (ASA) was pelleted Davison #980 commercial cracking catalyst used previously (10). Its composition was Al_2O_3, 13.2%; Fe, 0.03%; sulfate, 0.30%; Na_2O, 0.02%; SiO_2, 86.44% by difference. Its surface area was 388 m^2/g. The zeolite (Z) catalyst was pelleted Davi-

TABLE 1

Experimental Conditions

	Amorphous silica-alumina catalyst		Zeolite catalyst	
	1-Butene tracer	1-Heptene tracer	1-Butene tracer	Toluene tracer
n-Hexadecane fractional conversion, X_c	0.346	0.346	0.770	0.770
Carbon-14 tracer conversion, X_r	0.871	0.99946	0.984	0.357
Time on stream (min)	25	25	25	25
Gas flow (cm³/min STP)				
n-Hexadecane	21	23	18	17
Tracer	0.060	0.23	0.050	0.094
Helium	137	152	117	108
Catalyst weight (g)	23.2	23.2	23.2	23.2
Catalyst volume (cm³)	38	38	44	44
Contact time (sec)	4	4	6	7
Reaction temp (°C)	372	372	372	372

son XZ-25 commercial cracking catalyst which contained rare earth exchanged X-type faujasite zeolite incorporated in a silica-alumina matrix (14). Its composition was Al_2O_3, 31%; Fe, 0.07%; sulfate, 0.40%; Na_2O, 0.05%; rare earth oxides plus SiO_2, 68.5% by difference. The surface area of the catalyst was 338 m²/g.

The n-hexadecane was purchased from the Matheson Chemical Company as "olefin-free" material of 99% purity. A check of its purity by GC analysis showed only a very small amount (<1%) of high-molecular-weight impurity. The radioactive [1-¹⁴C]1-butene and [1-¹⁴C]1-heptene were purchased from Baird Atomic, Inc. The toluene tracer was purchased from Nuclear Research Chemicals, Inc. It was labeled in the first position of the ring.

Calculation of P_a^i. The small amount of radioactive intermediate added to the n-hexadecane allowed two different types of information to be obtained. First, the percentage of radioactivity which ended up in each product from a tracer was taken as the percentage of that intermediate which formed the products.

Second, the percentage of each product formed from the intermediate of interest was obtained. The calculation of this percentage from the radiochemical data requires some assumptions as to the kinetics of the reactions. The cracking of n-hexadecane with subsequent secondary reactions is schematically represented by

$$C \xrightarrow{k_c} \text{all intermediates}$$
$$\downarrow k_1$$
$$a \xrightarrow{k_2} \text{all products}$$
$$\downarrow k_3$$
$$i$$
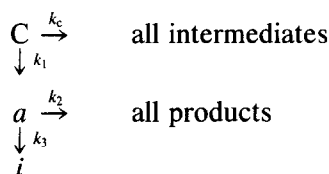
where C is n-hexadecane, a is the intermediate of interest, and i is the product of interest. The cracking of n-hexadecane and subsequent secondary reactions are assumed to follow apparent first-order kinetics, i.e., k_c, k_1, k_2, k_3 are first-order rate constants. The catalytic activities of the ASA and Z catalysts decrease with time on stream. However, the distribution of products was probably fairly constant over the time on stream (15, 16). Catalyst deactivation is absorbed into the rate constants which are based on conversions averaged

over the 25 min run time. The choice of first-order kinetics to describe the reaction sequences is supported by findings that cracking and secondary reactions of a number of hydrocarbons over silica-alumina and zeolite catalysts were found to obey first-order kinetics (15–20).

The fractional conversion of n-hexadecane, X_c, is related to k_c by

$$k_c = \frac{1}{t} \ln \gamma \qquad (5)$$

where t is the contact time and

$$\gamma = \frac{1}{1 - X_c}. \qquad (6)$$

Likewise, the fractional conversion, X_r, of the added tracer molecules which contain carbon-14 is related to k_2 by

$$k_2 = \frac{1}{t} \ln \rho \qquad (7)$$

where

$$\rho = \frac{1}{1 - X_r} \qquad (8)$$

and

$$X_r = \frac{(100 - \% \text{ tracer radioactivity at the reactor exit})}{100}. \qquad (9)$$

In a tracer experiment the product of interest, i, is formed from three sources:

(1) It is formed from the intermediate of interest, a_c, which is formed from the n-hexadecane. This portion of the product is called i_a.

(2) It is formed from the added tracer, a_r. This part of the product is called i_r.

(3) It is formed from intermediates other than the one of interest. This portion of the product is called i_b.

Thus,

$$i = i_a + i_b + i_r. \qquad (10)$$

Define i_c as

$$i_c = i_a + i_b. \qquad (11)$$

k_1 and k_3 appear in the equations for the intermediate A ($= a_r + a_c$) and the formation of the portion of the product (i_r) which contains carbon-14 from the radioactive intermediate (a_r);

$$\frac{dA}{dt} = k_1 C - k_2 A \qquad (12)$$

and

$$\frac{di_r}{dt} = k_3 a_r. \qquad (13)$$

These equations can be substituted into the equation

$$\frac{di_A}{dt} = k_3 A \qquad (14)$$

to give the product i_A formed from n-hexadecane via the intermediate a, which includes both the added tracer (a_r) and the portion of the intermediate formed from n-hexadecane (a_c).

The product distribution, given as moles of product per 100 mol of n-hexadecane cracked, was measured in an experiment in which no tracer was added. Thus, $i_r = 0$ for such experiments, and

$$i = i_a + i_b. \qquad (15)$$

The quantity sought, P_a^i, is obtained by combining the previous relations to obtain the equation:

$$P_a^i = \frac{100 i_a}{i_c} = \frac{100(i_A - i_r)}{i_c} \qquad (16)$$

where P_a^i is the percentage of the product i that had a as an intermediate. The intermediates reported here are the butenes (taken as a group) and 1-heptene for n-hexadecane cracking over ASA and 1-butene and toluene over the Z catalyst. Substitution of the expressions for i_A, i_r, and i_c into Eq. (16) and relating it to experimental quantities leads to the equation

$$P_a^i = \frac{N_a R \rho}{n N_i} \left[\frac{(\gamma - 1)\rho \ln \rho - (\rho - 1)\gamma \ln \gamma}{(\rho - \gamma)(\rho - 1) \ln \gamma} \right] \qquad (17)$$

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where N_a is the number of moles of intermediate a formed per 100 mol of n-hexadecane cracked, N_i is the number of moles of product i formed per 100 mol of n-hexadecane cracked, R is the percentage of radioactivity in product i, and n is the number of molecules of a reacting to form one molecule of i. N_a, N_i, R, and P_a^i are listed in Tables 2 and 3 for the tracers used in the experiments with the ASA and Z catalysts. n is assumed to be equal to one. γ and ρ can

be calculated from X_c and X_r given in Table 1 with the use of Eqs. (6) and (8).

For any given tracer experiment, γ, ρ, and N_a remain the same. For example, for the toluene tracer run over the zeolite catalyst, $\gamma = 4.356$, $\rho = 1.555$, $N_a = 2.66$, and $n = 1$. Substitution into Eq. (17) yields

$$P_{\text{toluene}}^i = \frac{2.267R}{N_i}. \qquad (18)$$

By substitution of the R and N_i values for

TABLE 2

n-Hexadecane Cracking over an Amorphous Silica-Alumina Catalyst

No.	Compounds	No. moles per 100 mol n-hexadecane cracked	Butene tracer group		1-Heptene tracer	
			Percentage of radioactivity	P_a^i	Percentage of radioactivity	P_a^i
1	Methane	0.59	0.041	7.1	0.008	0.03
2	Ethane	1.14	0.147	13	0.028	0.05
3	Ethylene	2.80	0.090	3.3	0.101	0.07
4	Propane	29.0	0.019	0.07	4.91	0.34
5	Propylene	55.5	1.84	3.4	4.51	0.16
6	i-Butane	77.0 ⎫	57.8 ⎫	63	56.0	1.50
7	n-Butane	16.6 ⎬	⎭		2.65	0.32
8	1-Butene	8.75 ⎫		—	1.19	0.27
9	i-Butene	24.6 ⎪	12.9	—	3.45	0.28
10	$trans$-2-Butene	15.1 ⎬		—	1.64	0.21
11	cis-2-Butene	10.2 ⎭		—	1.23	0.24
12	n-C$_5$	12.1	1.95	16	0.61	0.10
13	i-C$_5$	61.9	16.1	27	13.4	0.43
14	n-C$_6$	4.19	0.28	6.8	0.56	0.26
15	i-C$_6$	21.8	1.55	7.3	3.21	0.29
16	n-C$_7$ (not 1-heptene)	0.533 ⎫	0.16 ⎫	21	0.202	0.76
16a	1-Heptene	0.260 ⎭	⎭		0.054	—
17	i-C$_7$	10.1	2.50	25	4.27	0.86
18	n-C$_8$	0.86	0.06	7.1	0.035	0.08
19	i-C$_8$	2.27	1.14	51	0.37	0.32
20	n-C$_9$	0.30	0.003	1.1	0.015	0.10
21	i-C$_9$	1.11	2.214	20	0.095	0.17
22	n-C$_{10}$	0.24	0.028	12	0.010	0.08
23	i-C$_{10}$	0.37	0.094	26	0.029	0.15
24	i-C$_{11}$	0.16	0.014	9.0	0.028	0.35
25	Benzene	0.49	0.051	11	0.045	0.17
26	Toluene	0.70	0.17	25	0.24	0.69
27	Ethylbenzene	0.20	0.019	9.7	0.007	0.07
28	m- and p-Xylene	2.02	0.29	15	0.18	0.18
29	o-Xylene	0.74	0.076	11	0.009	0.02
30	C$_9$ aromatics	4.11	1.14	28	0.69	0.33
31	C$_{10}$ aromatics	3.30	0.73	23	0.64	0.38
32	Unknown	0.74	0.68	93	0.045	0.12
33	Coke	78.9	7.77	10	—	—

TABLE 3

n-Hexadecane Cracking over a Zeolite Catalyst

No.	Compounds	No. moles per 100 mol n-hexadecane cracked	1-Butene tracer		Toluene tracer	
			Percentage of radioactivity	P_a^i	Percentage of radioactivity	P_a^i
1	Methane	0.682	0.022	0.16	0	0
2	Ethane	0.786	0.101	0.66	0	0
3	Ethylene	2.39	0.143	0.31	0	0
4	Propane	13.8	0.546	0.20	0	0
5	Propylene	13.6	1.34	0.50	0	0
6	i-Butane	36.5	16.4	2.30	0	0
7	n-Butane	8.38	27.0	16.7	0	0
8	1-Butene	0.905	1.56	—	0	0
9	i-Butene	2.81	1.48	2.70	0	0
10	trans-2-Butene	3.81	2.92	3.93	0	0
11	cis-2-Butene	3.27	2.90	4.54	0	0
12	n-C$_5$	6.52	0.718	.056	0.111	0.04
13	i-C$_5$	48.6	14.1	1.49	0.406	0.02
14	n-C$_6$	3.78	0.306	0.41	0.047	0.03
15	i-C$_6$	31.9	3.26	0.52	0.529	0.04
16	n-C$_7$	2.32	0.174	0.38	0.116	0.11
17	i-C$_7$	19.7	2.49	0.65	0.492	0.06
18	n-C$_8$	0.74	1.56	10.7	0	0
19	i-C$_8$	11.2	1.49	0.68	0.971	0.21
20	n-C$_9$	0.53	0.012	0.12	0.106	0.45
21	i-C$_9$	8.21	0.774	0.48	1.65	0.46
22	n-C$_{10}$	0.33	0.004	0.06	0.157	1.08
23	i-C$_{10}$	0.60	0.018	0.15	0	0
24	i-C$_{11}$	0.43	0.020	0.24	0.154	0.81
25	Benzene	1.41	0.070	0.25	0	0
26	Toluene	2.66	0.244	0.43	64.3	—
27	Ethylbenzene	0.60	0.018	0.15	0	0
28	m- and p-Xylene	3.48	0.651	0.96	5.65	3.68
29	o-Xylene	1.67	0.178	0.55	1.30	1.76
30	C$_9$ aromatics	8.38	1.27	0.77	8.80	2.38
31	C$_{10}$ aromatics	6.56	0.955	0.75	4.00	1.38
32	Unknown	2.17	0.172	0.41	1.02	1.07
33	Coke	204	17.1	0.43	10.1	0.11

each product into Eq. (18), the percentage of each product formed via toluene was calculated as listed in the last column of Table 3.

Equation (17) can be used to calculate P_a^i for the other papers in this series (7–11). Once P_a^i is calculated for at least one product of a run, $\alpha_a^i(\max)$ for that run can be calculated from Eq. (3).

RESULTS AND DISCUSSION

The product distributions from the crack-ing of n-hexadecane over the ASA and Z catalysts are given in the third column of Tables 2 and 3, respectively. The product distributions for the ASA catalyst follows closely that reported by Hightower and Emmett (10). Seven additional groups of compounds were distinguished in our work for a total of 68 groups with the ASA catalyst and 49 with the Z catalyst. These groups were combined into the 33 reported here. The product distribution for the Z catalyst was considerably different than for

the ASA catalyst. As with gas oil cracking (21), the olefin content (not shown separately in Tables 2 and 3, but given in reference 12) of the products was much larger for the ASA catalyst than for the Z catalyst. With the ASA catalyst, more than one-third of the carbon atoms were found in olefins, while only 1 carbon atom in 10 was in an olefin in the Z catalyst product. The Z catalyst formed slightly more paraffins and twice as much aromatic product as the ASA catalyst on a basis of products formed per 100 mol of n-hexadecane cracked. The Z catalyst had 2.5 times as much cracked material forming coke as the ASA.

Thermodynamic equilibrium was established among the C_4 and C_5 olefins over the ASA (10, 22). Over the Z catalyst these olefins were not equilibrated. Equilibrium was not established between the normal and isoparaffins over either catalyst. The ratio of isobutane to n-butane at equilibrium at 372°C is 2:3. For the ASA catalyst the ratio was found to be 5:1. For the Z catalyst the ratio was 4.4:1. Isopentane and n-pentane also were not produced at their equilibrium value of 2:1. The ratio over the ASA catalyst was 9:1, while the ratio over the Z catalyst was 9.5:1. There were 12 and 25 mol of aromatic compounds per 100 mol of n-hexadecane cracked over the ASA and Z catalysts, respectively. Thermodynamic equilibrium was established among the four aromatic isomers: p-xylene, m-xylene, o-xylene, and ethyl-benzene over the ASA catalyst.

Amorphous silica-alumina—1-butene tracer. The results from the addition of 0.285 mol% of [1-^{14}C]1-butene tracer to n-hexadecane cracked over the amorphous silica-alumina catalyst are listed in Table 2. Although 1-butene was added as the carbon-14 tracer compound, it isomerized so rapidly to an equilibrium mixture of 1-butene, cis- and trans-2-butene, and isobutene that, in effect, the four butene isomers taken as a group were the tracer. The fourth column in Table 2 gives the percentage of radioactivity in each product. This is the

percentage of the butene group forming the product. As expected, most of the butene group reacts to form n- and isobutane (57.8%). A fairly large percentage (16.1%) of the butene group forms iso-C_5 compounds. There is 12.9% of the butene group passing through the reactor without reacting. Coke is formed from about 7.8% of the butenes. The rest of the butene group, about 5.4%, is spread among the other products.

The fifth column on Table 2 gives the P_a^i values for the butene group, i.e., the percentage of each product formed from the butene group. Although an important reaction of the butenes is hydrogenation to form n- and isobutane (63% of these paraffins are formed from butenes), the butenes are also important in the formation of significant amounts of almost all the products. The butenes build into the iso-compounds better than into the normal compounds. Product numbers 19 (i-C_8) and 32 (unknown) have unusually high P_a^i values (51 and 93%, respectively) suggesting these products may be dimers or trimers of the butenes [n = 2 or 3 in Eq. (17)].

Significant percentages (10 to 25%) of the aromatic compounds are formed from butenes. This is in line with the propylene and pentenes results as shown in Table 4. Ethylene was found to make a negligible contribution. The 1-pentene tracer data in reference 10 were used to calculate the results

TABLE 4

Percentage of Aromatics and Coke Formed from Olefins over the Amorphous Silica-Alumina Catalyst

Product	Olefin tracers			
	Ethylene[a]	Propylene[a]	Butene group	Pentene[a] group
Benzene	0	14	11	18
Toluene	0	12	25	23
Ethylbenzene	0	9	10	14
m-, p-Xylene	0	13	15	22
o-Xylene	0	12	11	20
Coke	0	3	10	8

[a] Calculated from data in ref. (10).

for the pentene group. Arguments for taking the pentenes as a group over the ASA catalyst are similar to those for the butenes. The results show that propylene, butenes, and pentenes participate in roughly 50% of the aromatic formation.

The percentage of coke formed from the C_2 through C_5 olefins is also shown in Table 4. Ten percent of the coke comes from butenes, which is higher than from propylene (3%) and similar to the pentene group (8%). The importance of these olefins as intermediates becomes more apparent when it is considered that more than one carbon atom per olefin molecule may become coke, i.e., that n is less than one in Eq. (17). For the formation of coke, n may be as low as $\frac{1}{3}$ for propylene, $\frac{1}{4}$ for butenes, and $\frac{1}{5}$ for pentenes, considerably increasing their P_a^i values.

Amorphous silica-alumina—1-heptene tracer. The results from the addition of 0.986 mol% of $[1\text{-}^{14}C]1$-heptene tracer to the n-hexadecane cracked over the amorphous silica-alumina catalyst are tabulated in Table 2. The 1-heptene did not isomerize to other C_7 olefins rapidly enough to come to equilibrium, so 1-heptene itself was the tracer rather than the group of heptenes. The lack of equilibration of the heptenes is due to the great cracking reactivity of the 1-heptene. Only 0.054% of the 1-heptene passed through the reactor unreacted. The percentage radioactivity in each product (column 6 of Table 2) indicates the percentage 1-heptene reacting to form that product. As with the butenes, more 1-heptene reacts to form iso-compounds than normal ones. Over half (56%) of the 1-heptene ends up as isobutane. Likewise, a comparable percentage of the 1-heptene probably ends up as propylene, but does not show up as radioactive propylene because the carbon-14 is in the first carbon position in the 1-heptene. The 1-heptene adsorbs on the catalyst forming a secondary carbonium ion which isomerizes by a methyl shift to form a tertiary carbonium ion. This is followed by β-scission cracking with hydrogen trans-

fer reactions taking place. The result is nonradioactive propylene and radioactive isobutane. This does not support the reaction scheme proposed by Nace (4) in which a ring intermediate is formed on the catalyst with equivalent carbon atoms. In that case the radioactivity should have been more prevalent in propylene and propane products than it is. Very little cyclization of 1-heptene occurs to form toluene (0.24%) or any other aromatic compound.

1-Heptene is not important as an intermediate in the formation of products, i.e., its P_a^i values are small for all products (Table 2, column 7). It is an intermediate in the formation of 1.5% of the isobutane, but otherwise contributes to less than 1% of the formation of any other product group. As with the butenes, 1-heptene makes a relatively larger contribution to the formation of iso-compounds than normal ones. As would be expected, it forms a larger percentage of toluene (0.69%) than it does any other aromatic compound. This lack of importance as an intermediate suggests that only a small amount of 1-heptene is formed in the cracking of n-hexadecane, since 1-heptene is very reactive once formed.

Zeolite—1-butene tracer. The results obtained from the addition of 0.278 mol% 1-butene tracer to the n-hexadecane cracked over the zeolite catalyst are listed in Table 3. The four butene isomers could not be combined into one tracer group, because equilibrium was not established among the isomers. The percentage radioactivity found in each product with the Z catalyst was roughly the same as that with the ASA catalyst. In general, more of the 1-butene reacted to form iso-compounds than the corresponding normal compounds.

The P_a^i values for the 1-butene tracer over the Z catalyst (Table 3, column 5) are much smaller than those over the ASA catalyst indicating that secondary reactions involving 1-butene are much less significant over the Z catalyst. The 1-butene enters into the formation of only 16.7% of the n-butane product. The P_a^i value for the per-

centage of n-C_8 compounds formed from 1-butene (10.7%) is relatively high indicating these products may be dimers of the butenes [$n = 2$ in Eq. (17)]. Even though 17% of the 1-butene went to form coke, less than half a percent of the coke had 1-butene as an intermediate.

Zeolite—toluene tracer. The results obtained from the addition of 0.555 mol% toluene tracer to n-hexadecane cracked over the zeolite catalyst are listed in Table 3. Over the Z catalyst 35.7% of the added toluene tracer reacted, while only 5% reacted over the ASA catalyst. Of the toluene that reacted over the zeolite catalyst, 28% went to coke and 50% was alkylated. An unusual feature of the compound formation via toluene is that some of the toluene appears to be methylated to form xylenes, etc. Of the alkylated toluene about 40% formed xylenes and about 50% went to trimethylbenzenes (*12*). More likely the toluene was alkylated by butenes and larger olefins followed by cracking of these alkyl chains leaving only methyl groups on the benzene ring.

The low P_a^i values for the toluene tracer experiment (Table 3, column 7) indicate that toluene is not a significant intermediate in the formation of other aromatic compounds. Only a small amount (1 to 4%) of the aromatic compounds have toluene as a precursor. Comparison of the P_a^i values for the run made over ASA catalyst by Hightower and Emmett (calculated P_a^i values from data in ref. *10*) with the values obtained with the Z catalyst show that toluene forms a larger percentage of the aromatic products over the Z catalyst. The values for P_a^i over the Z catalyst versus the ASA catalyst for m-, p-xylenes, o-xylene, C_9 aromatics, and C_{10} aromatics are 3.68 vs 0.14, 1.76 vs 0.14, 2.38 vs 0.04, and 1.38 vs 0.18, respectively.

CONCLUSIONS

In accord with other work on similar systems, it was found that more paraffins, aromatics, and coke and less olefins were formed per mole of n-hexadecane cracked over the zeolite catalyst than over the amorphous silica-alumina catalyst. The olefins (C_3 to C_5) are important intermediates in the reactions over amorphous silica-alumina, but as indicated by the 1-butene tracer, they are much less involved in the formation of products over the zeolite catalyst. From the 1-heptene tracer results, it was concluded that C_7 and olefins of higher carbon number are not as prominent in the formation of products from n-hexadecane cracking as the C_3 to C_5 olefins. Whether the importance of the olefins as intermediates reaches a maximum with the C_5 or the C_6 olefins has not been determined. Aromatics do not enter into secondary reactions to form other products to very much extent over either the amorphous silica-alumina catalyst or the zeolite catalyst, e.g., toluene is an intermediate in the formation of only a small amount (1 to 4%) of other aromatics over the zeolite catalyst. The contribution of toluene to the formation of other aromatic products is, however, about 10 times larger over the zeolite catalyst than over the amorphous silica-alumina catalyst.

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