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Catalytic Cracking of *n*-Hexadecane. IV. The Formation and Behavior of Aromatics over a Silica–Alumina Catalyst¹

Joe W. Hightower and P. H. Emmett

Contribution from the Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland. Received October 15, 1964

Some secondary reactions in the *n*-hexadecane–aluminosilicate system at 372° have been examined in an integral reactor with C-14 tracers in the presence of an inert helium diluent. The reactions of eight different primary products (ethylene, propylene, propane, pentene-1, *n*-heptane, *n*-decane, benzene, and toluene) were traced and their importance in determining the final product distribution assessed. The small paraffins were quite unreactive, but their reactivity increased markedly with molecular weight. Ethylene also showed little activity, but olefins with three or more carbon atoms underwent extensive alkylation, isomerization, polymerization, and cracking. Both propylene and pentene-1 participated extensively in the formation of all aromatics formed during the cracking of *n*-hexadecane, but only a small fraction of the alkyl aromatics was formed by direct alkylation of benzene or toluene. The single exception so far noted is the alkylation of benzene with propylene to form cumene. The radioactivity of the cumene was nearly as high as that of the benzene used as tracer. Most, if not all, paraffins above C₂ were formed by hydrogen transfer to the olefin of corresponding carbon number. The pentene isomers were found in thermodynamic equilibrium with each other, and radioactivity introduced into one of these rapidly equilibrated throughout all.

Introduction

A complex hydrocarbon mixture is obtained when pure *n*-hexadecane, a typical paraffinic oil, is cracked over an acidic silica–alumina catalyst. This final

product distribution is a composite of primary products produced initially from the *n*-hexadecane and of secondary products produced by further reactions of certain primary products, such as olefins. Van Hook and Emmett^{2–4} used C-14 tracers to investigate the quantitative importance of some secondary reactions (polymerization, isomerization, alkylation, and cracking). They also presented evidence supporting plausible routes for the formation of aromatics, a class of products whose formation is not clearly understood in light of the generally accepted carbonium ion theory of catalytic cracking.⁵ In this paper quantitative data from tracer experiments about other secondary reactions in hexadecane cracking are presented. Additional evidence as to the routes for aromatic formation and behavior is also given.

Small amounts (0.1 to 1.0 mole %) of eight C-14 labeled primary products (ethylene, propylene, propane, pentene-1, benzene, toluene, *n*-heptane, and *n*-decane) were mixed, in separate experiments, with a stream of helium saturated with *n*-hexadecane and passed at 372° through an integral reactor filled with a commercial silica–alumina cracking catalyst. The products were analyzed and separated by gas chromatography for radioactivity measurements.

Experimental

The over-all experimental scheme was similar to that used by Van Hook² and will be discussed only briefly.

(2) W. A. Van Hook, Doctoral Thesis, The Johns Hopkins University, Baltimore, Md.

(3) (a) W. A. Van Hook and P. H. Emmett, *J. Am. Chem. Soc.*, **84**, 4410 (1962); (b) *ibid.*, **84**, 4421 (1962).

(4) W. A. Van Hook and P. H. Emmett, *ibid.*, **85**, 697 (1963).

(5) H. H. Voge, "Catalysis," Vol. 6, P. H. Emmett, Ed., Reinhold Publishing Corp., New York, N. Y., 1958, Chapter 5.

(1) Taken from the doctoral thesis of J. W. Hightower and presented in part at the Third International Congress on Catalysis, Amsterdam, July 1964.

Table I. Description of Radiochemicals

Compound	Position of C-14	Sp. act. as purchased, mc./mmole	Sp. act. after dilution, mc./mmole
Ethylene	1	1.2	0.66
Propylene	1	1.6	0.40
Propane	1	1.6	0.49
Pentene-1	1	0.62	0.62
<i>n</i> -Heptane	1	0.065	0.065
<i>n</i> -Decane	1	3.3	0.78
Benzene	Uniformly labeled Ring	2.78	0.14
Toluene		1.00	0.15

Table II. Gas Chromatographic Scheme

Operation	Column (code)	Packing	Column length, ft.	Column temp., °C.	Column pressure, p.s.i.g.	Carrier flow, cc./min.	Amount of sample added	Fraction analyzed
a	Al ₂ O ₃	40-60 mesh activated Al ₂ O ₃	12	130	25	41.4	3 cc.	Gas
				160	20	29.0	1 cc.	C ₁ -C ₄
b	D (Perkin-Elmer)	Tetraisobutylene on Celite	9	40	17	25.6	1 cc.	Gas C ₄ -C ₆
c	A (Perkin-Elmer)	Diisodecyl phthalate on Celite	12	40	20	33.6	10 μl.	Liquid C ₁ -C ₇
d	A (Perkin-Elmer)	Diisodecyl phthalate on Celite	12	100	20	29.7	30 μl.	Liquid C ₇ -C ₉
e	A (Perkin-Elmer)	Diisodecyl phthalate on Celite	12	130	25	37.3	30 μl.	Liquid C ₅ -C ₁₀
f	74346 (Beckman)	Silicone 550 on firebrick	6	190	25	45.2	10 μl.	Liquid C ₁₀ -C ₁₆

Reactor System. The apparatus consisted of a helium carrier gas supply, a *n*-hexadecane bubble saturator, trace injector systems for radioactive gases and liquids, the reactor itself, and finally product traps. Catalyst regeneration and coke analysis trains were also provided.

A stream of helium at 1 atm. pressure (158 cc./min.) bubbled through a *n*-hexadecane saturator (210°, 101 mm. vapor pressure) and joined in a heated line a second helium stream (10 cc./min.) to which had been added a small amount of a liquid or gaseous tracer. This helium-hexadecane-tracer mixture entered a vertically mounted Pyrex reaction chamber containing Vycor chips for a preheater and 23.2 g. (38-cc. bulk volume) of Davison pelleted commercial cracking catalyst, the same type as used by Van Hook.² The maximum time of contact was 5.1 sec. A steel block furnace surrounded by exploded mica was maintained at 372 ± 1° by a Thyatron resistance controller. The hydrocarbon products were collected in a series of three traps (two at -195° and a third at about -215°). Hydrogen was the only reaction product not trapped and therefore not included in the analysis.

Before each experiment, all parts of the system were allowed to achieve temperature equilibrium with helium flowing over the catalyst and through the product traps. The two helium streams were switched to their respective saturators and the reaction products collected for exactly 25 min. The saturators were then by-passed with the helium continuing to purge the reactor of any adsorbed uncoked by-products for an additional 15 min.

The product traps were warmed to room temperature, and the gases were collected in 1-l. bottles by displacement of water which had been saturated with NaCl and outgassed under vacuum. The liquid fraction was weighed to the nearest milligram, and the volume of water displaced by the gases was noted. Both frac-

tions were saved for gas chromatographic and C-14 analysis. It was found that certain gases (particularly olefins) dissolved more readily than others in the salt solution, thus distorting any product distribution determined in this manner. The product distribution given in the third column of Table III was determined by expanding the gaseous fraction of a nonradioactive run directly into an evacuated 2-l. bulb and using this for analysis. Van Hook² has shown that the product distribution remains remarkably constant from run to run when the catalyst is carefully regenerated between runs.

After each run the catalyst was regenerated by burn-

ing off the coke deposit in a stream of purified air at ca. 500° for at least 24 hr. The exhaust gases were passed over a CuO catalyst (750°) to oxidize any CO or remaining hydrocarbon to CO₂ which was then absorbed in saturated barium hydroxide, the resulting carbonate precipitate being weighed and retained for radioactivity measurement.

All taps in the system, even those in transfer lines heated to 220° in order to prevent condensation of *n*-hexadecane, were greased with small amounts of Dow Corning "high-vac" silicone grease which is reported to be stable at this temperature.

Materials. "Olefin-free" *n*-hexadecane purchased from the Matheson Chemical Co. was reportedly 99% pure. It was further purified by vacuum distillation at 3 mm. through a 53-plate Todd column 90 cm. long, the middle third being used. Chromatographic analysis showed only one small peak, which is probably due to a small amount of branched hexadecane, eluting just before the *n*-hexadecane peak.

All eight C-14 tracers were purchased from Nuclear Research Chemicals, Inc. Table I contains the pertinent information about each. In most cases statements by the manufacturer that the compounds were of "highest purity" were accepted, and a few checks by a dilution technique for radioactive impurities indicated their statements were correct.

Chromatography. All reaction products were analyzed by a Beckman GC 2A gas chromatograph employing a thermal conductivity detector and helium carrier gas. Table II gives the analytical scheme for six chromatographic operations; the 60 identified peaks are shown in Figure 1, and the numbers correspond to the names in Table III. Qualitative analysis was made mainly on the basis of standard reference samples, but artificially constructed mixtures, infrared and mass spectrometric spectra of eluent peaks, and

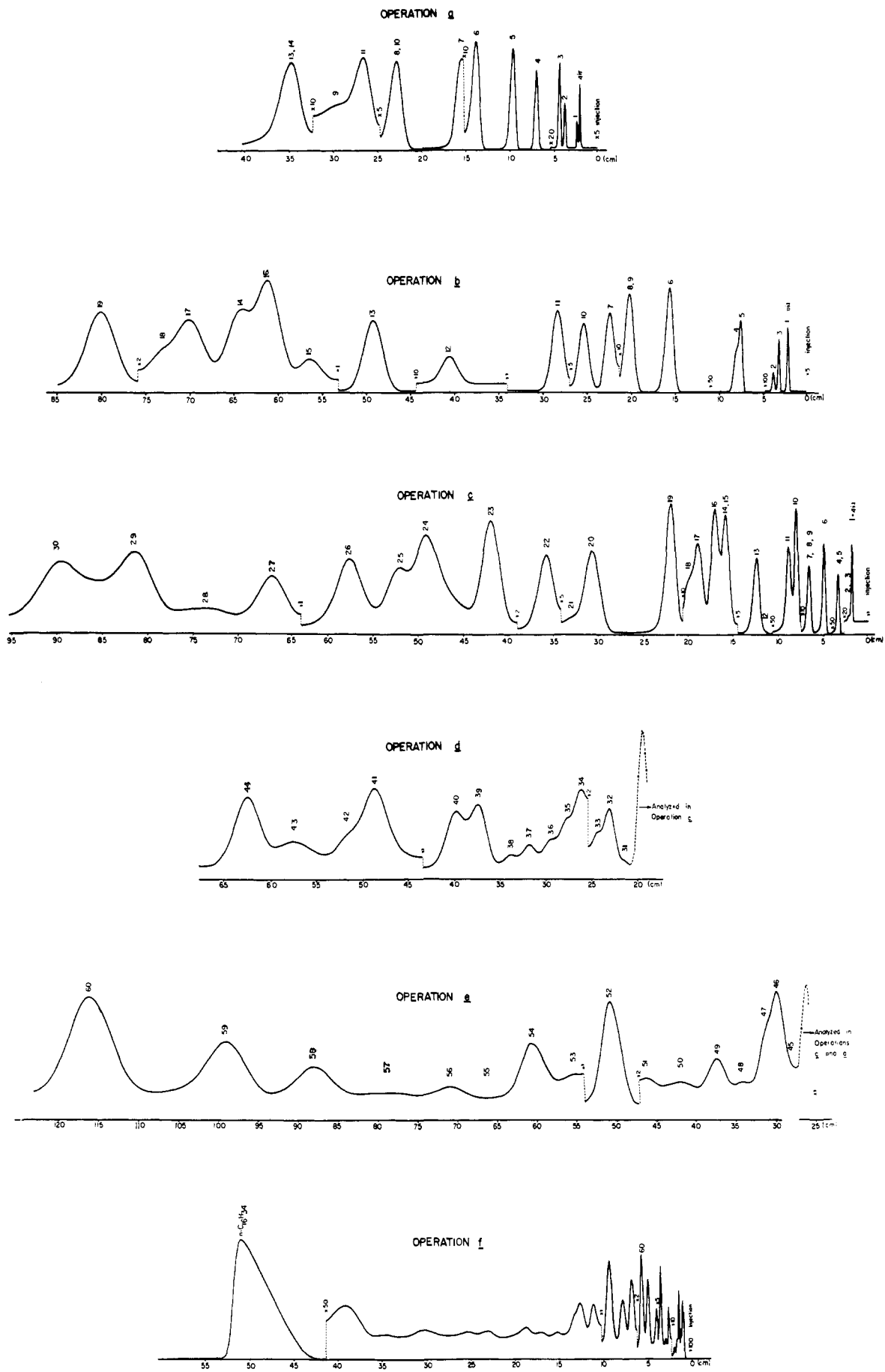


Figure 1. Sample chromatograms. Peak numbers refer to Table III; operations refer to Table II.

Table III. Results of C-14 Tracer Experiments in the Catalytic Cracking of *n*-Hexadecane

Peak no.	Compound	Moles/100 moles cracked	—0.10% ethylene*—		—0.10% propylene*—		—0.11% pentene-1*—	
			Activity, %	$\alpha^{12}\text{C}_2\text{H}_4$	Activity, %	$\alpha^{13}\text{C}_3\text{H}_6$	Activity, %	$\alpha^{13}\text{C}_5\text{H}_{10}$
1	Methane	0.59	0.012	0.00063	0.019	0.059	0.027	0.101
2	Ethane	1.14	2.367	0.04000	0.145	0.230	0.098	0.191
3	Ethylene	2.80	91.648	1.00000	0.331	0.214	0.333	0.265
4	Propane	29.03	1.046	0.00110	39.475	2.460	1.614	0.124
5	Propylene	55.51	0.491	0.00027	30.702	1.000	2.490	0.100
6	Isobutane	77.02	0.631	0.00025	7.389	0.174	9.991	0.283
7	<i>n</i> -Butane	16.55	0.105	0.00019	1.090	0.119	1.255	0.169
8	Butene-1	8.75						
9	Isobutene	24.64						
10	<i>trans</i> -Butene-2	15.08	0.452	0.00024	5.475	0.167	5.011	0.190
11	<i>cis</i> -Butene-2	10.20						
12	3-Methylbutene-1	1.17	0.235	0.00019	2.402	0.114	0.496	0.942
13	Isopentane	36.85					38.254	2.310
14	<i>n</i> -Pentane	3.96					5.672	3.190
15	Pentene-1	1.49	0.115	0.00029	0.834	0.123	0.670	1.000
16	2-Methylbutene-1	6.84					3.735	1.215
17	<i>trans</i> -Pentene-2	4.66	0.011	0.00005	0.579	0.157	2.710	0.910
18	<i>cis</i> -Pentene-2	1.96						
19	2-Methylbutene-2	17.04	0.108	0.00019	1.011	0.108	7.138	0.932
20	2,3-Dimethylbutane, 2-methylpentane	9.68	0.143	0.00040	0.836	0.137	1.699	0.337
21	Cyclopentane	1.33						
22	3-Methylpentane	6.15	0.106	0.00052	0.400	0.118	0.807	0.292
23	<i>n</i> -Hexane, hexene-1, 2-methylpentene-1	3.73	0.058	0.00047	0.248	0.120	0.456	0.272
24	Hexene-2, 3-methylpentene	5.10	0.075	0.00033	0.622	0.161	0.769	0.246
25	4,4-Dimethylpentene-1	1.86						
26	2,4-Dimethylpentane	3.14	0.081	0.00079	0.360	0.207	0.464	0.329
27	3,3-Dimethylpentane	0.99	0.005	0.00017	0.099	0.181	0.122	0.276
28	4,4-Dimethylpentene-2	0.33	0.078	0.425	0.048	0.321
29	3-Methylhexane, 2,3-dimethylpentane	2.12	0.506	0.432	0.215	0.225
30	3-Methylhexane	2.35	0.563	0.433	0.233	0.220
31	2-Methylhexene-1, 2,2,4-trimethylpentane	0.17	0.419	0.385	0.286	0.324
32	<i>n</i> -Heptane, heptene-1	1.10	0.149	0.398	0.097	0.320
33	2-Methylhexene-2	0.70				
34	Heptene-2, 3-ethylpentene-2	0.68	0.109	0.398	0.160	0.499
35	Benzene	0.49	0.057	0.466		
36	2,2,3,3-Tetramethylbutane	0.22	0.097	0.484	0.165	1.010
37	2,4-Dimethylhexane, 2,5-dimethylhexane	0.22	0.136	0.317	0.137	0.396
38	2,3-Dimethylhexane	0.14	0.129	0.322	0.150	0.461
39	2-Methylheptane, 2,3,4-trimethylpentane	0.77	0.176	0.372	0.182	0.472
40	3-Methylheptane	0.72	0.051	0.383	0.093	0.855
41	<i>n</i> -Octane, octene-1	0.68	0.137	0.348	0.296	0.928
42	Octene-2, octene-3	0.18	0.082	0.171	0.125	0.321
43	2,3,5-Trimethylhexane	0.24	0.039	0.239	0.059	0.435
44	Toluene	0.70	0.047	0.484	0.052	0.659
45	2,3-Dimethylhexane, 4-ethylheptane	0.04	0.030	0.276	0.051	0.580
46	2-Methyloctane	0.46	0.449	0.368	0.905	0.914
47	3-Methyloctane	0.28	0.148	0.339	0.268	0.802
48	2-Methyloctene-1	0.09	0.037	0.276	0.025	0.227
49	<i>n</i> -Nonane, nonene-1	0.30	0.037	0.276	0.025	0.227
50	2,5-Dimethyloctane	0.18	0.198	0.440	0.220	0.600
51	Ethylbenzene	0.20	0.307	0.436	0.426	0.745
52	<i>m</i> -Xylene, <i>p</i> -xylene	2.02	0.542	0.496	0.697	0.785
53	5-Methylnonane	0.19
54	<i>o</i> -Xylene	0.74
55	Cumene	Trace
56	<i>n</i> -Decane	0.24
57	2-Methyldecane	0.16
58	<i>n</i> -Propylbenzene	0.65
59	Mesitylene	1.28
60	<i>sec</i> -Butylbenzene	1.97
...	Coke	78.90	2.312	...	3.501	...	11.330	...

correlations between observed and tabulated properties of homologous series of hydrocarbons proved helpful

in some cases. In general, quantitative analysis was made from the observed peak areas as determined by

Table III (Continued)

Peak no.	—0.11% propane*—		—0.94% heptane*—		—0.79% decane*—		—0.70% toluene*—		—0.66% benzene*—	
	Activity, %	$\alpha^i C_3H_8$	Activity, %	$\alpha^i C_7H_{16}$	Activity, %	$\alpha^i C_{10}H_{22}$	Activity, %	$\alpha^i C_7H_8$	Activity, %	$\alpha^i C_6H_6$
1	0.039	0.0195	0.001	0.00010	0.008	0.00037	0.0265	0.00212	0.0007	0.000340
2	0.127	0.0328	0.010	0.00044	0.037	0.00097	0.0105	0.00044	0.0034	0.000100
3	0.076	0.0080	0.009	0.00016	0.025	0.00026	0.0203	0.00034	0.0099	0.000120
4	98.718	1.0000	0.111	0.00019	0.200	0.00021	0.0339	0.00005	0.0034	0.000004
5	0.477	0.0025	0.203	0.00018	0.427	0.00023	0.0811	0.00007	0.0035	0.000002
6	0.093	0.0004	0.326	0.00021	0.933	0.00036	0.1467	0.00009	0.0077	0.000003
7	0.080	0.0014	0.045	0.00013	0.143	0.00026	0.0408	0.00012	0.0042	0.000009
8	0.199	0.0010	0.158	0.00013	0.621	0.00032	0.0736	0.00006	0.0056	0.000003
9										
10										
11										
12	0.030	0.0002	0.087	0.00011	0.381	0.00030	0.0971	0.00012	0.0025	0.000002
13										
14	0.011	0.0003	0.125	0.00050	0.214	0.00052	0.0202	0.00008	0.0021	0.000006
15										
16										
17	0.006	0.0003	0.019	0.00037	0.117	0.00053	0.0227	0.00016	0.0018	0.000009
18										
19	0.016	0.0003	0.026	0.00008	0.255	0.00045	0.0406	0.00011	0.0017	0.000003
20	0.023	0.0006	0.029	0.00013	0.286	0.00086	0.0176	0.00008	0.0007	0.000002
21										
22	0.012	0.0005	0.021	0.00017	0.153	0.00074	0.0149	0.00011	0.0008	0.000004
23	0.000	0.0000	0.077	0.00101	0.077	0.00062	0.0090	0.00011	0.0000	0.000000
24	0.018	0.0008	0.021	0.00015	0.144	0.00062	0.0151	0.00010	0.0003	0.000002
25										
26	0.022	0.0021	0.023	0.00035	0.079	0.00075	0.0247	0.00037	0.0019	0.000002
27	0.017	0.0052	0.009	0.00046	0.022	0.00066	0.0039	0.00018	0.0002	0.000004
28	0.004	0.00051	0.006	0.00054		
29	0.049	0.00112	0.032	0.00045	0.0007	0.000006
30	0.072	0.00150	0.040	0.00050		
31	97.448	1.00000	0.040	0.00061	0.0065	0.00016	0.1803	0.00309
32										
33										
34	0.344	0.02520	0.018	0.00082	0.0058	0.00041	96.4201	1.000000
35	0.118	0.01740	0.235	0.01424	0.0064	0.00061		
36	0.050	0.01100	0.010	0.00134	0.0021	0.00045		
37	0.059	0.00800	0.011	0.00084	0.0035	0.00047	0.1688	0.015700
38								
39	0.028	0.00180	0.011	0.00042	0.0076	0.00046	0.0316	0.001380
40	0.021	0.00140	0.011	0.00044	0.0048	0.00031	0.0154	0.000746
41	0.017	0.00099	0.043	0.00151	0.0117	0.00065
42								
43	0.006	0.00122	0.006	0.00078	95.0040	1.00000
44	0.0932	0.00644	0.019	0.00080				
45	0.072	0.00407	0.027	0.00050	0.0087	0.000337
46								
47								
48								
49	0.016	0.00259	0.498	0.04920	0.0217	0.00342	0.0096	0.001075
50	0.010	0.00265	0.019	0.00327	0.0186	0.00504	0.0098	0.001800
51	0.011	0.00261	0.025	0.00385	0.0254	0.00612	0.1580	0.027000
52	0.025	0.00054	0.129	0.00175	0.6006	0.01295	0.0768	0.001275
53								
54	0.016	0.00106	0.119	0.00478	0.1964	0.01254	0.0376	0.001710
55								
56	0.007	0.00139	93.814	1.00000	0.0110	0.00217
57	0.007	0.00054						
58			0.128	0.00588	0.3353	0.01953	0.0911	0.003770
59	0.012	0.00046	0.122	0.00286	0.1009	0.00377	0.0460	0.001190
60	0.017	0.00043	0.123	0.00186	0.6785	0.01630	0.4035	0.006900
...	0.037		0.202	...	0.395	...	2.2570	...	0.7198	...

planimetry, although peak heights under carefully controlled conditions were used to measure the low molecular weight gases. Calibration was effected with standard reference compounds; the sensitivity of those few peaks for which standard reference compounds were not available was determined from sensitivity vs. retention time plots.

Although analysis was carried out only through C_{10} , it may be noted from operation f, Figure 1, that there

were at least five significant peaks with higher molecular weight than C_{10} . The peak just preceding the *n*-hexadecane peak was identical with the one present as an impurity in the starting material. It should also be observed that in many cases complete resolution of neighboring peaks was not achieved, and occasionally there was complete overlap of two peaks, e.g., *n*-paraffins and their α -olefins above C_6 .

Counting Technique. The counting technique was

different from either of those used by Van Hook.² A small amount of oxygen bled into the exit gas of the gas chromatograph just ahead of a glowing platinum catalyst enabled the separated hydrocarbons to be burned to CO₂. Ten interchangeable traps stuffed with glass wool and cooled to -195° were used to trap the CO₂. By this technique as many as ten "peaks" could be trapped from one sample injection into the gas chromatograph.

For static counting the CO₂ in the traps was transferred by vacuum distillation into an evacuated Baird Atomic VPC-164 proportional vapor flow counter which was then filled to atmospheric pressure with methane quench gas. Counting characteristics include a reported efficiency of 95% and a normal background of 100 c.p.m. (counts per minute). This latter figure was reduced by lead shielding to 40 c.p.m. The plateau at the operating voltage of 3800 v. had a slope of 2% per 100 v. Other Baird Atomic counting apparatus used included a 319A high voltage power supply, a PA-224 amplifier, a 123A Abacus scaler and timer, and a 432A research rate meter whose output was fed into a Leeds and Northrup Speedomax G recorder.

Each sample was counted statically for 30 min., with a 15-min. background count preceding each measurement. By removing a known fraction of certain highly radioactive samples when necessary, the amount of radioactivity measured in the counter was kept below 1500 c.p.m. in each sample. This ensured that there was no loss of efficiency in the counter owing to poor resolution of pulses which occurs at high counting rates.

Radioactivity in the coke was measured in the following way. Acidification of the barium carbonate precipitate in a gas sampling device produced CO₂, a 0.5-cc. sample of which was injected into the gas chromatograph and trapped in the usual fashion for radioactivity measurement.

Results and Discussion

The results of the integral reactor experiments may be divided into three parts: the product distribution, nonaromatic tracer studies, and aromatic tracer studies.

Product Distribution. The number of moles of each product per 100 moles of *n*-hexadecane cracked at 372° is given in column 3 of Table III. Although the over-all product distribution is similar to that of Van Hook and Emmett,^{3a} there are a few differences. Some of the high molecular weight peaks which they identified as being C₁₀ and C₁₁ *n*-paraffins were actually shown to be C₉ and C₁₀ aromatics. The total number of moles of products formed per 100 moles of *n*-hexadecane cracked, however, was in close agreement: 368 in the present work and 376 in the former. Carbon-hydrogen balance among the products is quite good and indicates that less than 1% of the over-all hydrogen from the *n*-hexadecane admitted probably was given off as H₂.

Complete thermodynamic equilibrium is established among all the C₄ olefins, the C₅ olefins, and the C₈ aromatics. Table IV compares the fraction of each of the products within a particular group with the equilibrium fraction from Rossini's calculations.⁶ Although

Table IV. Fractions of C₄ and C₅ Olefins and C₈ Aromatics Formed Compared with Equilibrium Fractions

Compound	Fraction observed in products	Fraction at equilibrium
Butene-1	0.15	0.14
Isobutene	0.42	0.42
<i>trans</i> -Butene-2	0.26	0.26
<i>cis</i> -Butene-2	0.17	0.18
2-Methylbutene-2	0.51	0.47
3-Methylbutene-1	0.04	0.03
2-Methylbutene-1	0.21	0.27
<i>trans</i> -Pentene-2	0.14	0.12
<i>cis</i> -Pentene-2	0.06	0.07
Pentene-1	0.04	0.04
<i>p</i> -Xylene	0.68	0.22
<i>m</i> -Xylene		0.48 (0.70)
<i>o</i> -Xylene	0.25	0.23
Ethylbenzene	0.07	0.07

lack of chromatographic resolution made separation of all olefins above C₅ impossible, it is doubtful that complete thermodynamic equilibrium is established among all olefins of higher molecular weight owing to the extreme amount of isomerization which would be necessary to form some of them.

As has been long known, thermodynamic equilibrium is not established among all the different paraffins of a given carbon number, for in most cases there is a large excess of the branched species. For example, the equilibrium ratio of isobutane to *n*-butane at 372° is about 2:3; the observed ratio is about 5:1.

A few compounds present in minor quantities were identified as having quaternary carbon atoms, a type of compound generally not found among the products of catalytic cracking. It is, of course, possible to form these species either by alkylation (*t*-butyl carbonium ion with isobutylene followed by hydrogen addition to form 2,2,3,3-tetramethylbutane) or by two successive alkyl shifts to the same carbon atom which has been the charge center of a carbonium ion.

It is significant to note that fairly large quantities of aromatics (8.1 moles per 100 moles of *n*-hexadecane cracked) are produced, and the tracer experiments described in the next section give clues concerning plausible routes for their formation.

Nonaromatic Tracer Studies. The results of the six integral reactor experiments using nonaromatic tracers are given in columns 4-15 of Table III, two columns of information being given for each experiment. The first in each series entitled per cent activity gives the per cent of the total radioactivity present in each product compound and directly indicates the relative importance of the various secondary reactions of a given radioactive tracer. Table V gives a more general summary of the importance of different types of reactions for each tracer.

In the second column for each experiment are tabulated the ratios of the specific activities (the radioactivity in counts per minute per cc. (mole) of a given hydrocarbon) of each product *i* at the bed exit to that of the traced primary compound *a* at the bed exit. This ratio is a direct indication of the importance of any or all reactions, *a* → *i* (by any mechanism) in determining the exit concentration of *i* as compared with all

(6) F. D. Rossini in "Physical Chemistry of Hydrocarbons," Vol. 1, A. Farkas, Ed., Academic Press, Inc., New York, N. Y., 1950, Chapter 9.

Table V. Summary of Reactions Each Tracer Underwent

	C ₂ H ₄	C ₃ H ₆	C ₅ H ₁₀	C ₈ H ₈	C ₇ H ₁₆	C ₁₀ H ₂₂	C ₇ H ₈	C ₆ H ₆
Unreacted	91.7	30.7	0.7	98.7	97.4	93.8	95.0	96.4
Cracked	0.0	0.5	20.8	0.2	1.3	4.9	0.7	0.4
Hydrogenated	2.4	39.5	43.9
Isomerization to isoparaffins	0.5
Olefins of same C no.	14.1	0.5
Nonaromatic alkylation	3.6	24.0	6.2	0.5	0.3
Aromatized	..	1.8	3.0	..	0.3	0.9
Alkylated to higher aromatics	2.0	2.5
Formed coke	2.3	3.5	11.3	0.1	0.2	0.4	2.3	0.7

other sources of *i* (i.e., not from or through *a*). In other words, the numbers plotted in the second column are defined as

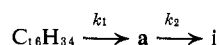
$$\alpha_a^i = \frac{\text{(specific activity of } i \text{ at exit)}}{\text{(specific activity of } a \text{ at exit)}}$$

If all the product *i* were formed from some reaction involving *a*, the maximum value $\alpha_a^{i_{max}}$ would then obtain. $\alpha_a^{i_{max}}$ may be calculated⁷ for an integral reactor by making reasonable assumptions of reaction orders, rate constants, etc., and the fraction of *i* produced by reactions involving *a* becomes

$$\text{fraction } i \text{ from } a = \frac{\alpha_a^{i_{obsd}}}{\alpha_a^{i_{max}} n}$$

where *n* is the number of moles of *a* necessary to form 1 mole of *i*.

In the first paper of Van Hook and Emmett,^{3a} $\alpha_a^{i_{max}}$ was calculated for the two reactions



under three different conditions, and the values lie between 1 and 2. A fourth set of conditions shows that if $k_1 \gg k_2$ and both reactions are zero order with large dilution of radioactive *a** by nonradioactive *a* formed from C₁₆H₃₄

$$\alpha_a^{i_{max}} = \ln \left(\frac{k_1 l}{V_a(o)} \right)$$

where $k_1 l$ is the total volume of *a* produced by cracking per unit time along the bed of length *l*, and $V_a(o)$ is the volume of tracer compound *a** added per unit time. Since $k_1 l \gg V_a(o)$, then $\alpha_a^{i_{max}}$ may have values as large as 2-3.

It is reasonable to assume that in all the tracer experiments described herein, the values of $\alpha_a^{i_{max}}$ between 1 and 3 when only a single molecule of *a* is involved in forming a molecule of *i*. At this point each experiment will be discussed in detail.

Ethylene. From column 4 of Table III it is immediately obvious that only 8.4% of the ethylene admitted reacted in any way to form other compounds. The most important reaction was that of hydrogenation to ethane, but assuming an $\alpha_a^{i_{max}}$ value of 2, only 2% of the ethane formed during the reaction is formed through a process involving ethylene. Although there was a significant amount of radioactivity in the coke, apparently only a negligible amount of polymerization to C₄ compounds occurred. Since the α -values for most peaks through number 27 were extremely small, radioactivity measurements were not carried beyond

(7) W. K. Hall, R. J. Kokes, and P. H. Emmett, *J. Am. Chem. Soc.*, 79, 2983 (1957).

that point. In Figure 2 the α -values for three series of hydrocarbons (*n*-paraffins, olefins, branched olefins and paraffins) are plotted as functions of carbon number.

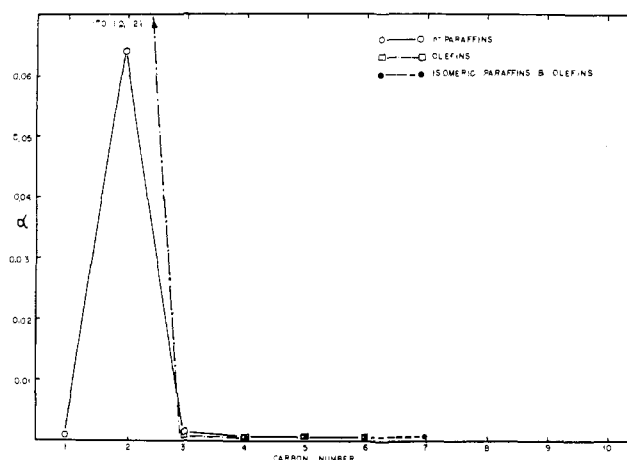


Figure 2. Ethylene tracer in *n*-hexadecane cracking.

Another ethylene tracer experiment was carried out under similar conditions with the exception that propylene was substituted for *n*-hexadecane as the material to be "cracked." As one would expect,⁸ propylene underwent extensive reaction to form products from C₁ to C₅ (the liquid fraction was too small to be analyzed), but the α -values were very similar to those obtained when *n*-hexadecane was cracked. There was only about 2% hydrogenation and negligible polymerization, and the radioactivity in the coke was almost identical with that from the previous experiment. (It should perhaps be noted that the results here obtained are not in contradiction to those published by Kokes, Tobin, and Emmett.⁹ The ethylene used by those authors was many times more radioactive and at a higher partial pressure than that used in the present experiments.)

In a third experiment nonradioactive ethylene diluted in helium was passed over the catalyst. Although a small amount of coke was formed, there was no other detectable reaction. When the helium was replaced with a hydrogen diluent, almost 90% of the ethylene was hydrogenated to ethane, but again no other reaction (except a small amount of coking) was observed.

(8) F. E. Shephard, J. J. Rooney, and C. Kemball, *J. Catalysis*, 1, 379 (1962).

(9) R. J. Kokes, H. Tobin, and P. H. Emmett, *J. Am. Chem. Soc.*, 77, 5860 (1955).

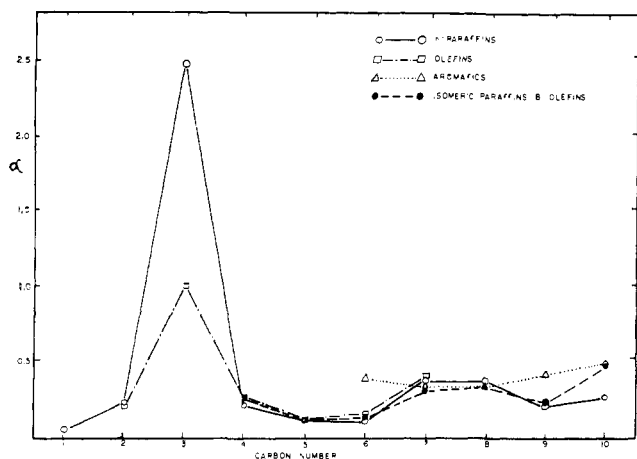


Figure 3. Propylene tracer in *n*-hexadecane cracking.

One would expect ethylene to be quite unreactive under cracking conditions owing to the relative instability of the ethyl carbonium ion. The hydrogenation of ethylene to ethane in the presence of an atmosphere of hydrogen may have been catalyzed by metallic impurities, for analysis of the catalyst showed 0.3% Fe. If this were the case, the hydrogenation may go through an ethyl radical adsorbed on the metal and not through a carbonium ion at all. Others,¹⁰ however, have also reported that ethylene is hydrogenated over silica-alumina catalysts in an atmosphere of hydrogen.

It should be noted that the small α -value for ethane shows that no more than 2% of the ethane formed comes from ethylene regardless of whether the mechanism involves the hydrogenation of the ethylene on metallic impurities or the chemisorption of ethylene to form an ethyl carbonium ion. The data are consistent with the occasional formation of a surface ethyl carbonium ion during the cracking of *n*-hexadecane with a resulting hydrogenation to ethane by hydrogen transfer from *n*-hexadecane or with a substantially irreversible decomposition of the ethyl carbonium ion to form ethylene.

Propylene. Figure 3 shows the α -values vs. carbon number plot obtained when propylene was used as a tracer in *n*-hexadecane cracking. Although this experiment is identical with one carried out by Van Hook and Emmett, there are some differences between the two results. Whereas they found the α -values for propane to be 1.75, our results were 2.45 and 2.46 in two separate experiments. Also, they found that the α -values continued to increase for *n*-paraffins from C₆ to C₁₂, while in the present experiments these values went through a maximum at C₇ or C₈ and then decreased. This discrepancy is due to the fact that the peaks they originally identified as *n*-paraffins above C₉ were in reality aromatics. In both experiments the aromatics analyzed showed a rather large amount of radioactivity.

In another experiment carried out at 430°, only a small amount of radioactive propylene was added. Because the radioactivity was so dilute, it was possible to count only the propane, propylene, and coke. In this case the α -value for propane was again 2.35, and since this value is only 4% lower than that obtained at 372°, the process by which propane is formed from

(10) G. Parravano, E. F. Hammel, and H. S. Taylor, *J. Am. Chem. Soc.*, **70**, 2269 (1948).

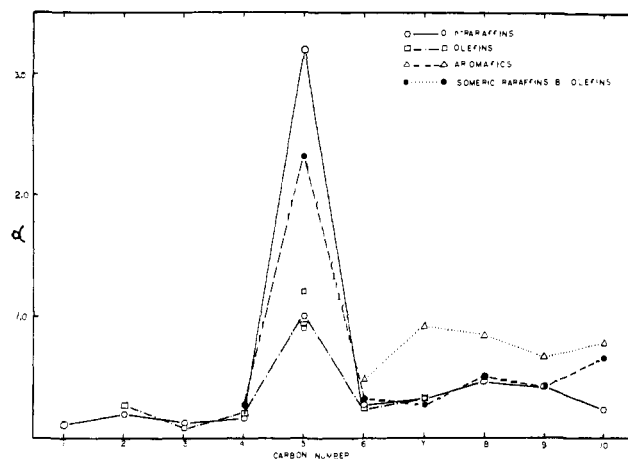


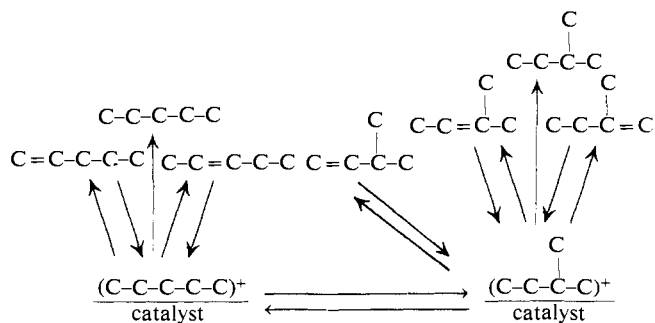
Figure 4. Pentene-1 tracer in *n*-hexadecane cracking.

propylene must be essentially independent of temperature in this region.

The high α -value for propane indicates that most (if not all) of the propane is formed in some way from propylene. A significant fraction (20 to 50%) of all aromatics formed during cracking must involve propylene somewhere along the way.

Pentene-1. As was true with propylene, when pentene-1 was added as a tracer in *n*-hexadecane cracking, a significant amount of radioactivity was found in all products as shown in Figure 4. Both *n*-pentane and isopentane showed large α -values (3.2 and 2.3, respectively), indicating that most of each was formed from the respective olefins. All isolated pentenes, whether normal or branched, had specific activities approximately equal to that of pentene-1 in the products. Again the aromatics had high α -values, and the aliphatic α -values appeared to go through a maximum at C₈. The high radioactivity of the coke indicates that a large amount of it was formed from pentene-1.

Both the equal specific activities and the thermodynamic equilibrium of all pentenes imply that each must be in rapid equilibrium with species on the surface of the catalyst, as illustrated by the following skeletal scheme. The iso- and *n*-pentanes are then formed irreversibly by hydrogen transfer to the corresponding branched or straight chain carbonium ion.



From the α -values for the aromatics, it is seen that from 15 to 30% of all aromatics are formed in ways which involve pentene-1.

Melik-Zade and co-workers¹¹⁻¹³ studied the forma-

(11) M. M. Melik-Zade, M. R. Musaev, and I. G. Safaraliev, *Azerb. Neft. Khoz.*, **39**, No. 8, 33 (1960); *Chem. Abstr.*, **55**, 25225 (1961).

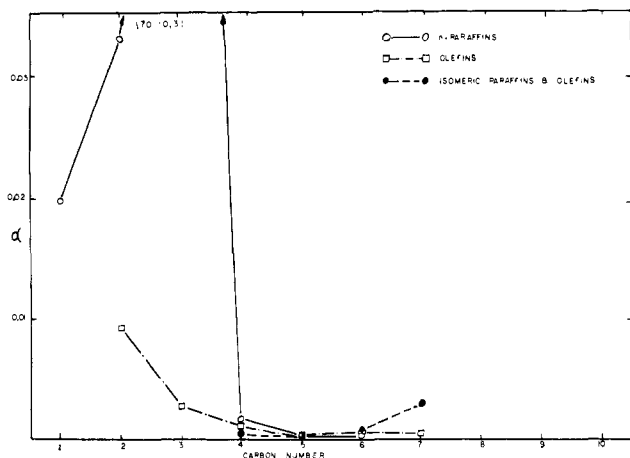


Figure 5. Propane tracer in *n*-hexadecane cracking.

tion of coke and aromatics by passing C-14 *n*-pentylbenzene (both by itself and in *n*-hexadecane) over a silica-alumina catalyst at 450°. Their results indicate that the *n*-pentyl group was cleaved at the ring and became pentene-1 which reacted to give a wide range of products. When the C-14 was in the α -position of the *n*-pentyl group, the coke contained a relatively high fraction of the radioactivity. However, when the C-14 was in the benzene ring, the radioactivity in the resulting benzene was quite high but that in the coke was low. This certainly is in agreement with the present results, for our C-14 pentene-1 produced a large amount of coke, but as will be seen, neither benzene nor toluene formed much coke.

Propane. The α -value plot for propane is shown in Figure 5, and this experiment duplicated one by Van Hook and Emmett. The main difference between the two results lies in the estimated over-all reactivity of propane; they reported that 20% of the propane reacted to form other compounds, whereas in the present work less than 2% of the added radioactive propane reacted in any way. The α -value for propylene is 0.0025 compared with 0.12 which they reported. It is suggested that since the propane used by the former authors was prepared by hydrogenating radioactive propylene, perhaps about 20% of the propylene remained unsaturated. If this were the case, it would explain the apparent higher activity in their results than in the present case. Also there is the possibility that some of their radioactive propylene on admission with hydrogen to a nickel catalyst at room temperature might have formed some dimers or trimers which later in the cracking run could have cracked to propylene and other products. Unfortunately, because of difficulties entailed in handling the very radioactive tracer, the propane actually produced by Van Hook and Emmett^{3a} by hydrogenation of radioactive propylene over nickel at room temperature was not analyzed for residual propylene or for possible propylene polymers.

As one would expect for a small paraffinic hydrocarbon, propane possesses only negligible reactivity under cracking conditions. There is not significant dehydrogenation of propane to form propylene, and

(12) M. M. Melik-Zade, M. R. Musaev, and I. G. Safaraliev, *Azerb. Neft. Khoz.*, 39, No. 11, 42 (1960); *Chem. Abstr.*, 55, 23988 (1961).

(13) M. M. Melik-Zade and M. R. Musaev, *Azerb. Neft. Khoz.*, 40, No. 2, 42 (1961); *Chem. Abstr.*, 56, 5016 (1962).

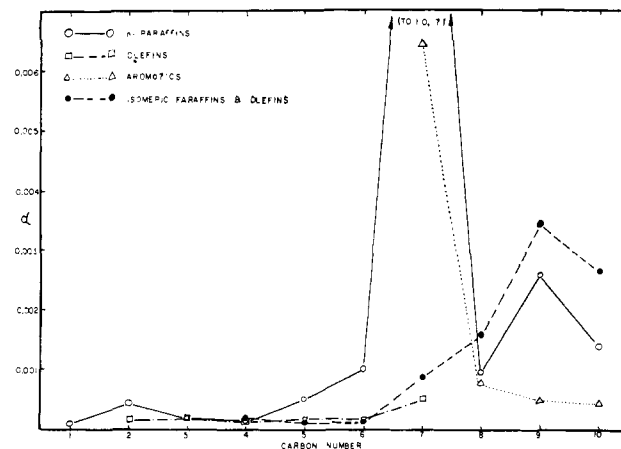


Figure 6. Heptane tracer in *n*-hexadecane cracking.

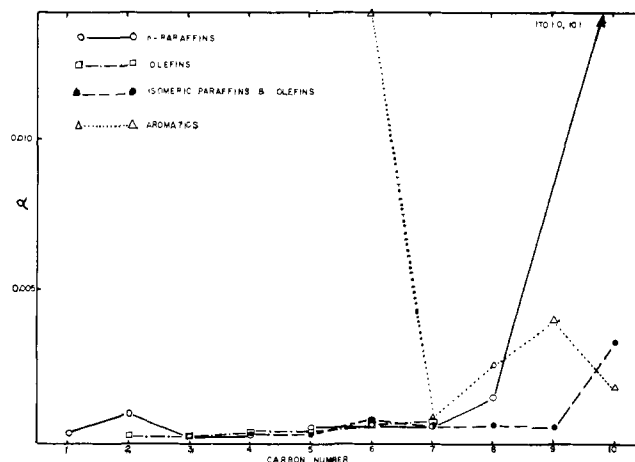


Figure 7. Decane tracer in *n*-hexadecane cracking.

any propane formed during the cracking reaction proceeds through the remainder of the catalyst bed as a relatively inert compound; *i.e.*, propane does not participate appreciably in secondary reactions during cracking.

***n*-Heptane.** Figure 6 shows the α -value plot for *n*-heptane; and again this experiment is a duplicate of one by Van Hook and Emmett.^{3a} As was true in the previous case, there was considerably more radioactivity in the products of the earlier experiment (a factor of three) than in the present case. Probably this is also due to their incomplete hydrogenation of heptene-1 to the heptane which was used as a tracer.

In comparison with other aromatics, there is a slight specificity for *n*-heptane to form toluene rather than other aromatics by dehydrocyclization. Even so, less than 1% of all the toluene formed during the cracking reaction is formed *via* this path. As was true with propane, *n*-heptane does not participate in secondary reactions to an appreciable extent.

***n*-Decane.** Although *n*-decane (see Figure 7 for α -value plot) is more reactive than *n*-heptane (by a factor of 2.5), still it is relatively inert when compared with *n*-hexadecane or olefins above C₂. The rather high α -value for benzene (0.014) is probably in error, for an experiment with radioactive benzene immediately preceded the decane tracer experiment, and traces of the benzene may have remained adsorbed on the walls

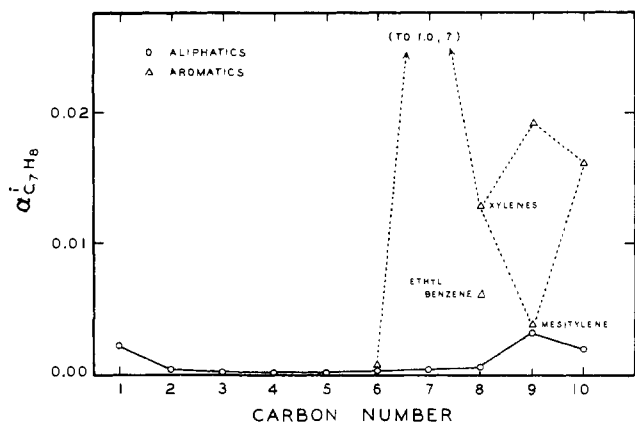


Figure 8. Toluene tracer in *n*-hexadecane cracking.

of the reaction system. Other aromatics have slightly high α -values because their chromatographic peaks are not completely resolved from the highly radioactive *n*-decane peak.

In both the decane and heptane experiments, the amount of tracer added (0.79 and 0.94 mole per 100 moles of *n*-hexadecane, respectively) was larger than the amount of each material normally formed in the reaction. Since there was little dilution of the radioactivity in the tracer compound, $\alpha_{a \max}^i$ for both cases must have a value close to unity. This means the α -values observed are roughly equal to the fraction of each product formed from the tracer.

The α -values for all products from C_1 through iso- C_9 are approximately equal (0.00056 ± 0.00020). One would expect this if the cracking products of *n*-decane are essentially the same as the products obtained from *n*-hexadecane cracking.

Aromatic Tracers. Thus far it has been shown that large fractions of aromatics are formed by reactions involving the olefins propylene and pentene-1, but less than 1% is formed by dehydrocyclization of paraffins such as *n*-heptane and *n*-decane. Another possible path for the formation of alkyl aromatics is *via* alkylation of small aromatics, *e.g.*, toluene or benzene.

Toluene. Figure 8 shows the α -value plot when toluene labeled in the α -position of the ring was used as a tracer. Since essentially no cracking of the ring occurred, there was negligible radioactivity found in the aliphatic hydrocarbons, and all these compounds have been averaged and plotted as a single line. Because of the fairly large radioactive toluene addition (compared to the toluene normally formed), $\alpha_{a \max}^i$ is again approximately unity. There was little dealkylation of the methyl group, as shown by the small α -value of the benzene peak. Although some alkylation to higher molecular weight aromatics did occur, still less than 2% of such compounds are formed from toluene. The higher α -values for the xylenes than for ethylbenzene indicate that it is easier to add a methyl group to the ring than to the existing methyl group in toluene.

Benzene. The α -value plot obtained when benzene was used as a tracer is given in Figure 9. The α -values for the aliphatic hydrocarbons were vanishingly small and were not even included in the figure. Again the large amount of benzene added fixes $\alpha_{a \max}^i$ near unity.

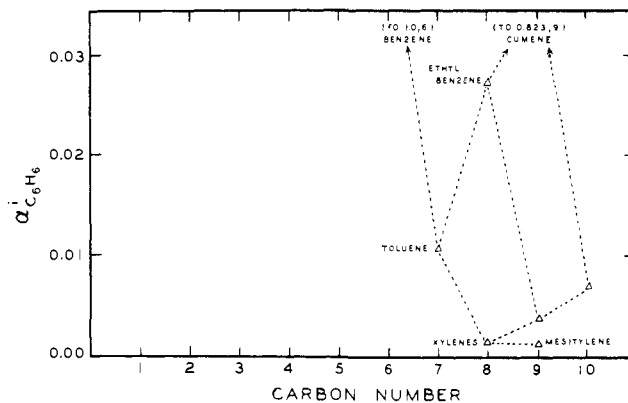


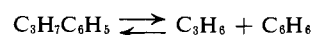
Figure 9. Benzene (0.66%) tracer in *n*-hexadecane cracking.

Toluene, the xylenes, and mesitylene all have small α -values indicating that alkylation of benzene with methyl groups is not a very important reaction. The larger α -values for ethylbenzene and cumene (0.027 and 0.82) show that alkylation of benzene by olefins (*e.g.*, $C_3H_6 + C_6H_6 \rightarrow C_9H_{10}$) does occur to an appreciable extent. Cumene normally is formed only in trace amounts among the products, but when the benzene partial pressure is increased by injecting various amounts of benzene together with the *n*-hexadecane, the peak corresponding to cumene is proportionally increased. This may be seen in Table VI in which the

Table VI. Increase in Cumene Caused by Addition of Benzene During Reaction

Benzene added, %	Benzene peak area (arbitrary units)	Cumene peak area (arbitrary units)
0.00	3.04	..
0.66	14.83	0.28
2.20	42.34	0.95
4.83	89.38	1.96

cumene chromatographic peak area (in arbitrary units) is compared with the benzene peak area for four experiments in which various amounts of benzene were added during the reaction. The equilibrium constant K_p for the reaction



is 0.363 at 372°, and a calculation of K_p from the partial pressures of benzene, propylene, and cumene at the exit of the reactor yields a value of 0.472. Within experimental error it appears that cumene is in equilibrium with benzene and propylene, and the high α -value for cumene indicates that most of it is formed from benzene. It is interesting to note that the peak areas of other aromatics are not affected by the addition of benzene during the reaction.

Ethylbenzene is formed slightly in excess of the amount which would be in equilibrium with benzene and ethylene, and thus alkylation of benzene could not have been the only source of its existence, even though the reversible nature of the reaction, though not equilibrated, could account for some of the radioactivity from the benzene entering the ethylbenzene.

Conclusions

Integral reactor tracer experiments on the secondary reactions of selected olefins, paraffins, and aromatics during the cracking of *n*-hexadecane have led to the following conclusions.

1. *Olefins*. (a) The alkylation, polymerization, and hydrogen-transfer reactions of olefins larger than ethylene are very important in determining the final product distribution. (b) Ethylene is essentially unreactive under cracking conditions, for no polymerization and little hydrogenation to ethane or coke formation occurs. (c) A very large fraction of all saturated products (75 to 100%) at least through C₅ are formed through the olefins (*e.g.*, propane from propylene; *n*- and isopentane from pentenes). (d) All olefins of a given carbon number at least through C₅ are in thermodynamic equilibrium with each other among the products, and radioactivity introduced into one of them is rapidly equilibrated throughout all. (e) Significant fractions (probably more than 50%) of all aromatics are formed in some way from the combination of small olefinic fragments on the surface of the catalyst. (f) The fraction of isomeric or normal hydrocarbons formed from both propylene and pentene-1 does increase directly with molecular weight above C₆, but it appears to go through a maximum around C₈ and then decreases.

2. *Paraffins*. (a) Normal paraffins through C₁₀ are very much less reactive than their corresponding olefins. (b) Dehydrogenation to form an olefin does not occur to any appreciable degree. (c) Neither dehydrocyclization of heptane to toluene nor dehydrocyclization of decane followed by dealkylation to form benzene are important reactions in the formation of aromatics.

3. *Aromatics*. (a) Under cracking conditions used in these experiments, neither the alkylation of benzene or toluene with a methyl group nor dealkylation of toluene to benzene occurred in appreciable amounts. (b) The only alkylation reactions which did occur were those in which an olefin was in equilibrium with benzene to form the corresponding alkyl aromatic (propylene and benzene to form cumene). The very small quantities of benzene normally formed in the cracking reaction made the equilibrium quantities of these alkyl aromatics very small.

4. *Coking*. A measure of the relative coking of each tracer may be obtained by comparing the percentages of the total radioactivity which entered the coke in each run. The following list shows the results relative to *n*-hexadecane which has been normalized to unity.

<i>n</i> -Hexadecane	1.00	Toluene	1.71
Propane	0.07	Ethylene	1.75
<i>n</i> -Heptane	0.15	Propylene	2.65
<i>n</i> -Decane	0.30	Pentene-1	8.58
Benzene	0.55		

Olefins are by far the most active compounds in forming coke. Alkyl aromatics appear to be second in coke-forming ability, followed by benzene and paraffins. Most of the coke appears to be formed not by alkylation of benzene or toluene into condensed polycyclic compounds on the surface, but rather by polymerization of small olefinic species.

The fact that the various isomeric pentenes occur at equilibrium in the reaction products whereas the saturated C₅ is largely in the form of isopentane suggests that the isomerization is much faster than hydrogen transfer in the present experiments at 372°. This is directly opposite to the conclusion reached by Shephard, Rooney, and Kembal⁸ in their study of the polymerization of propylene at and below 200° on a silica-alumina catalyst. They accounted for the absence of *n*-paraffins in their products by assuming that the polymers formed from propylene yielded branched carbonium ions and that these by hydrogen transfer were converted into branched paraffins before the isomerization to normal carbonium ions could occur. Possibly, the apparent contradiction between these two sets of results can be explained by hydrogen transfer having a lower temperature coefficient than isomerization on the silica-alumina catalysts. At any rate, it is quite evident that the pentene-1 used as a tracer is not preferentially rapidly converted to *n*-pentane as would be the case if hydrogen transfer were rapid compared to isomerization.

Acknowledgments. This work was supported by the United States Atomic Energy Commission under Contract Number AT (30-1)-2008, which also provided a salary for the student member of the contract, J. W. H.