is large compared with k_2 the rate at low temperature may be higher than the rate at high temperature.

We note that the preceding suggestion bears some relation to another process in which rates increase with decreasing temperature, the electrical conductivity of metals. Here the transmission of electrons increases with decreasing temperature because of decreased scattering by the vibrations of the environment.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, JOHNS HOPKINS UNIVERSITY, BALTIMORE 18, MD.]

Tracer Studies with Carbon-14. I. Some of the Secondary Reactions Occurring during the Catalytic Cracking of *n*-Hexadecane over a Silica–Alumina Catalyst

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Some secondary reactions in the *n*-hexadecane–aluminosilicate system at 372° have been examined in an integral reactor with carbon-14 tracers in the presence of an inert helium diluent. The reactions of the primary products propylene, propane, *n*-butane, 1-heptene and *n*-heptane were traced and their importance in determining the final product distribution assessed. Product and radioactivity analyses were made through carbon number twelve with the use of gas chromatography and static (carbon dioxide) counting, respectively. The results may be briefly summarized by pointing out that the tracer olefins, propylene and heptene, undergo as secondary reactions very extensive alkylation, isomerization, polymerization and cracking during the cracking of the hexadecane. Propylene seems to play an important part in the formation of aromatics and also in the formation of the higher saturated C_8- to C_{12}-hydrocarbons. On the other hand, the saturated tracer hydrocarbons propane, *n*-butane and *n*-heptane are relatively inactive during the hexadecane cracking runs and come through the reactor almost unchanged.

Introduction

The carbonium ion theory of catalytic cracking independently proposed by Greensfelder, Voge and Good[2] and by Thomas[3] in 1949 is now generally accepted by most workers in the field. The primary cracking products of any pure hydrocarbon feed predicted by the theory are, however, to some extent obscured by the products of the secondary reactions of the olefins and paraffins formed in the reaction. These secondary reactions include isomerization, hydrogenation, alkylation, polymerization and aromatization. The last of these reactions (aromatization) is not clearly understandable in the light of the present carbonium ion theory,[4] although the others follow as a direct consequence of the reactions of carbonium ions. In this paper are presented and discussed the results of some tracer experiments in which the quantitative importance of the secondary reactions, polymerization, isomerization, alkylation and cracking of some of the primary products have been assessed, and in which evidence is obtained relative to the plausible routes of aromatic formation.

In these experiments small amounts (0.06 mole % of gases, 0.9–1.5 mole % of liquids) of tagged primary products including propylene, propane, heptene-1, *n*-heptane and *n*-butane were mixed with a stream of *n*-hexadecane and helium and passed at 372° through an integral reactor filled with cracking catalyst. The products were analyzed gas chromatographically and counted.

Such a technique has been previously utilized by Andrianova and co-workers[5–8] in studies of isooctane cracking. However, their results are not amenable to precise interpretation because the inordinately high tracer to reactant ratios used by them lead to the suspicion that the steady state conditions on the catalyst surface were seriously affected by the added tracer compounds. Furthermore, analysis of their products was complete only through carbon number five; radioactive analysis of the higher cuts, including aromatics, were then grouped and averaged.

Experimental

Reactor System.—The apparatus consisted of helium carrier gas supplies, a hexadecane bubble saturator, trace injector systems for gases and liquids, the reactor itself and finally the product traps. Catalyst regeneration and coke analysis trains were also provided. The system was made of Pyrex.

Helium (stream I) was bubbled through the hexadecane saturator at about 215° after which it was joined in a heated transfer line by a second helium carrier flow (stream II) which had already passed through the tracer injector system. This last, for gaseous tracers, consisted of a motor-driven mercury leveling device made from 2-mm. capillary tubing fitted at the top with a 0.1-mm. restriction 2 cm long. It metered 0.01 cc./min. S.T.P. of the gaseous tracer into helium stream II. For liquid tracers, a long narrow bubbler, thermostated at an appropriate temperature, was used for adding the tracer to stream II.

The helium–hexadecane–tracer mixture entered the reaction chamber in which 23.2 g. (37-cc. bulk volume) of Davison pelleted commercial cracking catalyst[9] was supported with a plug of glass wool. The 25-mm. (o.d.) Pyrex reactor tube was supported in a vertically mounted steel block furnace 6" in diameter and 16" long. A glass thermocouple well ran through the center of the catalyst

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(1) Abstracted from part of the Doctoral thesis of W. A. Van Hook.

(2) B. S. Greensfelder, H. H. Voge and G. M. Good, *Ind. Eng. Chem.* **41**, 2573 (1949).

(3) C. L. Thomas, *ibid.*, **41**, 2564 (1949).

(4) H. H. Voge. Chapter 5 of "Catalysis," Vol. 6. "Hydrocarbon Catalysis," edited by P. H. Emmett, Reinhold Publishing Corp., New York, N. Y., 1958.

(5) E. A. Andreev, T. I. Andrianova, B. V. Klimenok, O. V. Krylova, S. Z. Roginskii and M. M. Sakharov, *Doklady Akad. Nauk SSSR*. **96**, 781 (1954), cited from *C. A.*. **49**, 7230c (1955).

(6) E. A. Andreev, T. I. Andrianova, O. V. Krylova and M. M. Sakharov, *Doklady Akad. Nauk SSSR*, **102**, 1119 (1955).

(7) S. Z. Roginskii and T. I. Andrianova, *Zhur. Obshchei Khim.*, **26**, 2151 (1956), cited from *C. A.*, **51**, 3973i (1957).

(8) T. I. Andrianova and S. Z. Roginskii. "Problemy Kinetiki i Kataliza, Akad. Nauk SSSR, Inst. Fiz Khim.." Soveshchanie, Moscov, 1956, Vol. 9. pp. 152–161; *C. A.* **53**, 7743c (1958).

(9) The catalyst analysis, as given through the courtesy of W. R. Briggs, W. R. Grace Research Center, Clarkville, Md., was 13.21% Al_2O_3, 0.03% Fe, 0.30% SO_4, 0.02% Na_2O and 86.44% silica (by difference). The surface area was 540 m.^{2}/g. and the pore volume 0.74 cc./g.

TABLE I
GENERAL CHROMATOGRAPHIC SCHEME

Operation	Column (code)	Packing	Temp., °C.	Flow of He carrier gas, cc./min.	Column length, m.	Analyzed
a	Al_2O_3	20/40 mesh Al_2O_3	50	38	4	Gas cut C_1–iC_4
b	D	Tetra isobutylene on Celite	30	27	2	Gas cut C_1–C_5
c	A	Dioctyl phthalate on Celite	60	53	2	Liq. cuts C_1–C_8 Gas cut C_6–C_8
d	A		122	89	2	Liq. cuts C_8–C_{11}
e	A		162	184	2	Liq. cuts C_{10}–C_{16}

bed which was approximately 15 cm. long and was situated in the center portion of the furnace. The 10- to 12-cm. portion of the tube immediately above the catalyst was filled with Vycor chips serving as a preheater. Gas flow was from the top of the tube to the exit at the bottom. Temperature was controlled with an electronic Thyratron device described by Benedict.[10] The bed temperature was uniform along its length to ±2° and at any given point uniform over any given time to ±1°.

At the exit of the reactor the gas flow entered a series of two tared product traps at −195° and one (untared) trap at −215 to −220° (solid nitrogen at a temperature corresponding to a pressure at the top surface of the trap of about 5 mm.). This last trap was provided to catch any methane that did not dissolve in the condensed hydrocarbons of traps I or II. Hydrogen, then, was the only gas not trapped and hence not analyzed.

In a run, the reactor tube at 372°, the hexadecane injector at *ca.* 215° and the traps at −195 and −215° were allowed to come to stable temperature equilibrium with flowing helium. After the flushing was complete, the flows were switched to the respective saturators and the products collected for (usually) 30 minutes, after which the catalyst was purged for another 30 minutes with helium in order to collect those products adsorbed on the catalyst surface but not yet coked.

The traps were allowed to warm to room temperature and the evolved gases collected in a 2-liter Erlenmeyer flask by displacement of water. The liquid product was crudely separated into two fractions by vacuum distillation (pot at room temperature, receiver at −195°); the volume of gas collected was noted, and finally the two liquid fractions were weighed to the nearest milligram. The product in the first trap had a very faint yellow color in all experiments. Since no colored compounds were found in the analysis, its origin is unknown. It was observed that this color was more pronounced in early preliminary experiments with *n*-hexadecane used as purchased without further purification.

At the end of every run the catalyst was regenerated by burning off the coke deposit in a stream of prepurified air (150–200 cc./min.) at 485–500° for at least 24 hours. Two tared desiccant tubes at the exit of the reactor dried the stream after which it flowed through 10–20 mesh CuO at *ca.* 800° to oxidize any CO to CO_2. The CO_2 was absorbed with Ascarite (non-radioactive runs) or saturated barium hydroxide solution (radioactive runs) and weighed.

The necessity of providing bypasses and a sampling facility made it necessary to include two stopcocks in the heated transfer line (*ca.* 230°) leading to the reactor. These were greased with a minimum quantity of Dow-Corning "high-vac" silicone grease which gave satisfactory performance with only very slight decomposition. The decomposition products should be mostly catalytically inactive silicates and related compounds which would deposit on the glass walls, preheater, etc., and thus not foul the catalyst. These assumptions were borne out in practice for no decrease in catalyst activity could be detected over a period of several months intermittent use.

Materials. ***n*-Hexadecane** was obtained from the Matheson Chemical Co., passed through silica gel and distilled, at 20-mm. pressure, in a 50-plate column packed with Pyrex helices. The middle third was retained (total temperature variation during this cut was less than 0.1°) and stored over silica gel. Physical characteristics were $n^{2.32°}_D$ 1.4330, m.p. 18.1°; reference values[11] are n_D 1.4345 (20°), 1.4325 (25°); m.p. 18.165°.

Propylene-1-C^{14} (1.23 mc./mmole) was purchased from Research Specialties Co. of Richmond, Cal. The manufacturer's specifications of > 99.9% purity were accepted. They were based on gas chromatograms submitted by the company.

Propane-1-C^{14} (1.23 mc./mmole) was prepared from propylene-1-C^{14} by room temperature hydrogenation over a nickel catalyst supported on kieselguhr and carefully reduced for 24 hours in a flow of prepurified hydrogen at 325°. Non-radioactive controls showed greater than 99.5% conversion to propane in one 5-minute reaction period in the static system. Three separate 15-minute reaction periods, using fresh hydrogen in each, alternated with 5- to 10-hour catalyst reductions, were performed with the radioactive sample. Analysis of the radioactive hydrogenated sample was not made for reasons of safety and economy. The same catalyst was later shown to give complete hydrogenation of heptene to heptane. In view of the precautions mentioned above, the assumption of essentially complete conversion to propane is probably warranted.

***n*-Butane-1-C^{14}** (1.0 mc./mmole) was obtained from the Orlando Research Co., Orlando, Fla. Manufacturer's specifications of better than 99.9% purity were accepted. The extremely low activity of the products in radiobutane experiments substantiate this assumption. Thus the activity of isobutane (a logical major impurity) in the exit gas of a cetane cracking run with n-$C^{14}{}_4H_{10}$ as tracer was 2×10^{-4} that of the exit *n*-butane.

1-Heptene-1-C^{14} (1.1 mc./mmole) was purchased from Research Specialties Co., Richmond, Cal. Manufacturer's specifications of greater than 99.9% purity based on gas chromatographic analysis were accepted. The sample was diluted to a specific activity of 0.1 mc./mmole with redistilled Matheson reagent grade heptene-1.

***n*-Heptane-1-C^{14}** (0.1 mc./mmole) was prepared by hydrogenating 1-heptene-1-C^{14} in a flow system over the catalyst previously described. In all, eight passes were made. Control experiments were again used to demonstrate completeness of reaction. Analysis here was by refractive index.

Chromatography.—The reaction products were analyzed gas chromatographically with a Perkin-Elmer model 154 Vapor Fractometer. The final analytical scheme is shown in Table I; and the forty-six identified peaks are listed in Tables II and III and shown in Fig. 1. Qualitative analysis was made on the basis of standard reference compounds, artificially constructed mixtures, infrared spectra of eluent peaks, and the observed and tabulated properties of homologous series. Quantitative analysis was made from the observed peak heights which were reproducible with careful control of operating variables. This pro-

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[10] M. Benedict, *Rev. Sci. Instr.*, **8**, 252 (1937).

[11] F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.

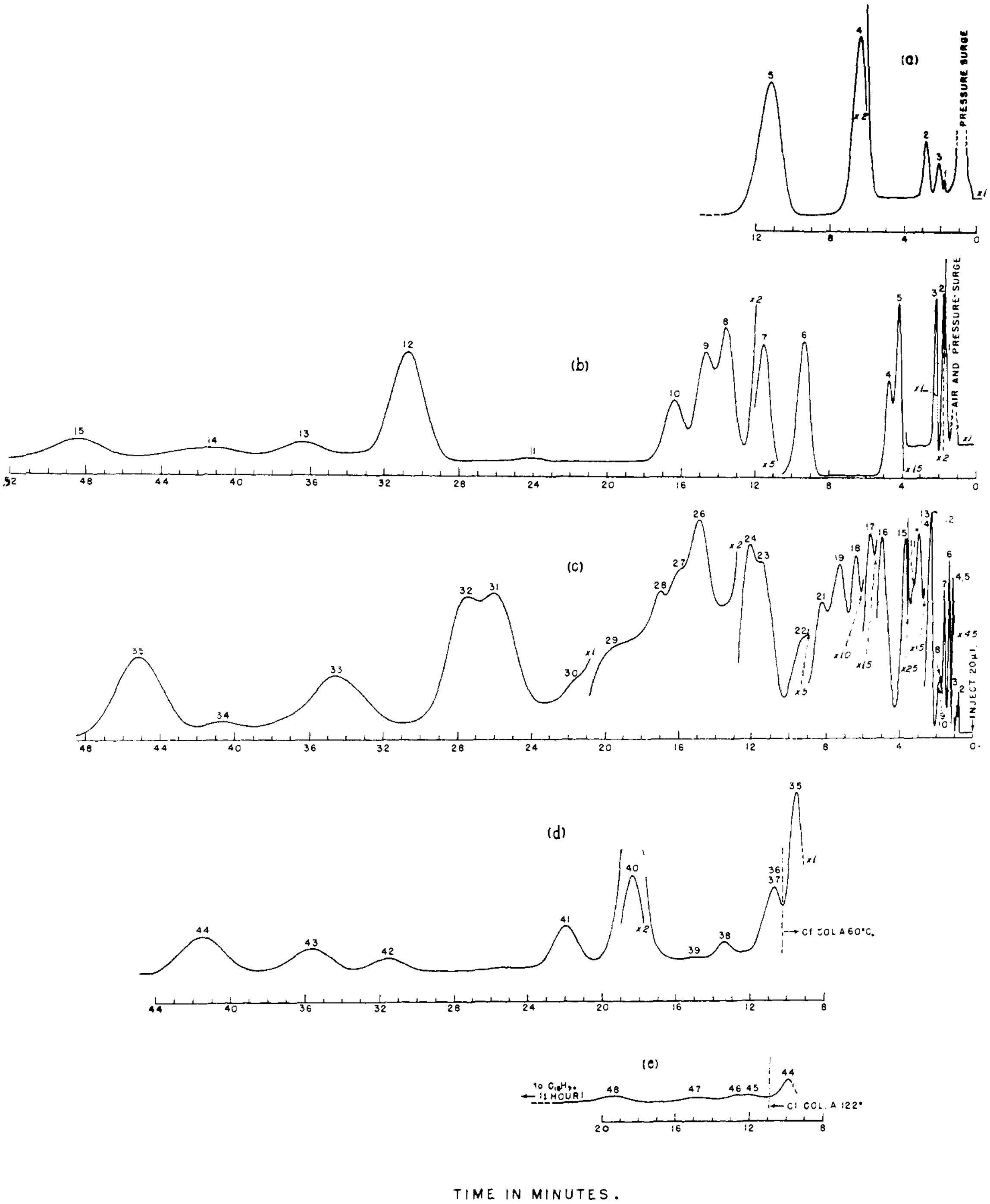

Fig. 1.—Sample chromatograms. Peak numbers refer to Table II; cut designations are as in Table I, as follows: a, gas cut on Al_2O_3 column, 50° (2 cc. S.T.P.); b, gas cut on D column, 30° (2 cc. S.T.P.); c, liquid cut I ("low boilers") on A column, 60° (20 μl.); d, liquid cut I on A column, 122° (20 μl.); e, liquid cut I on A column, 162° (50 μl.).

cedure was necessitated by the incomplete resolution of many peaks with the result that individual areas could not be measured. Calibration was effected with standard reference compounds; the sensitivity for those few peaks for which standard reference compounds were not available was determined from large scale retention time *vs.* sensitivity plots.

It may be noted that the analytical scheme is not sensitive enough at high retention times to detect the small amounts of C_{13}-, C_{14}- and C_{15}-hydrocarbons reported by other authors. Furthermore, the resolution of the instrument is much worse at high than at low retention times. Thus, it is likely that peaks represented as *n*-C-10, *n*-C-11 and *n*-C-12 may also contain some of the unresolved branched isomers. Finally in the analytical scheme, normal paraffins are not resolved from their α-olefins for carbon number six and above.

Counting Techniques.—Two separate counting techniques, A and B, were employed during the present work. The first, A, a modification of the liquid nitrogen trapping method already reported by Blyholder and Emmett,[12]

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[12] G. Blyholder and P. H. Emmett, *J. Phys. Chem.*, **63**, 962 (1959).

was used only for the chronologically first experiments, those using radio-heptene-1. The experimental procedure and apparatus for this A method was identical to that described by those authors with the following modifications: 1. The separated gases from the Vapor Fractometer were burned to CO_2 over a glowing platinum gauze before counting. A small amount of oxygen was bled into the exit gas flow from the Fractometer just ahead of the platinum catalyst to accomplish this. The oxidation was incorporated in the counting procedure to ensure that all samples would have uniform trapping tendencies, and also to avoid the high backgrounds resulting from difficulties in desorption of hydrocarbons from the counting chamber at the completion of a run.

2. The counting chamber and nitrogen reservoir was constructed from brass instead of Pyrex in order to effect better heat transfer.

3. Only one eluent peak was counted at a time, the remaining part of the chromatogram being vented. This technique resulted in a considerable increase in time and labor compared with the method of successive plateaus described by Blyholder[13] but affords much greater precision. Thus it was necessary to fractionate a separate sample for each counting operation. The size of the sample injected to the fractometer was adjusted whenever possible to maintain a roughly constant amount of trapped CO_2. Due to the finite vapor pressure of carbon dioxide at −195°, correction of counting rates to zero trapping time was necessary. This correction at the standard flows employed amounted to 1 to 2%/min.

Upon the acquisition of a new Tracerlab TGC-14 thin window counting tube, technique A was abandoned in favor of static gas counting, B. The hydrocarbons corresponding to the various eluent peaks were, as before, burned to CO_2 which was caught in specially designed narrow Pyrex traps at −195°. The CO_2 was then transferred by conventional techniques at a convenient time to the gas-tight counting system. The counting chamber, 98.5% of the total of the counting system volume, was separated from the counting tube by a thin (0.6–1.0 mg./cm.^{2}) aluminized Mylar window. The remaining 1.5% of the volume was a capillary circulation loop into which the CO_2 from the traps could be transferred by freezing. It was fitted with the necessary vacuum and flushing gas leads.

Counting in the gaseous state insured reproducible sample geometry as well as greater convenience and economy for long time counts. Furthermore, with the use of several traps more than one hydrocarbon for analysis could be obtained from each chromatographic run.

Both techniques, A and B, were demonstrated to be completely efficient and reproducible within the limits of measurement as judged by repeated trapping and counting.

Coke activity was determined by acidification of a weighed amount of barium carbonate precipitate followed by drying and counting the CO_2 in the usual fashion.

Results and Discussion

The results of these integral reactor tracer experiments are shown in Tables II and III. For each run the first column of data shows the total millimoles of any given product formed in that run. The product distribution indicated by these data will be discussed in the third paper of this series. Additional details relevant to all operating variables will be found in the second paper of this series together with a discussion of coke activities and coking rates and a presentation of experiments with a differential reactor. The specific activities found in the second column (in microcuries per millimole) are estimated to range between 5 and 10% in accuracy depending on the counting statistics. For the great majority of samples these were within 2% but were somewhat higher for some samples of low activity. The chromatographic error was some 2 to 3%. It may be noted that for computational purposes in Tables II and III we have carried extra digits in the first three columns for each run. These have been dropped in the fourth column, showing the specific activity ratios; this last column is the one in terms of which most of our results will be discussed. The third column, entitled fraction of total activity, needs no explanation. It directly indicates the relative importance of the various secondary reactions of the given radioactive tracer. It is interesting to summarize these data for a more direct comparison as shown in Table IV.

In the fourth column (Tables II and III) are tabulated the ratios of the specific activities of all products, i, at the bed exit, to that of the traced primary compound, a, at the exit. This ratio is a direct indication of the importance of any or all reactions, a→i, (any mechanism) in determining the exit concentration of i as compared to all other sources of i (*i.e.*, not from or through a). A term α^i_a may then be defined by the equation

$$\alpha^i_a = (\text{spec. act. of i at exit})/(\text{spec. act. of a at exit}) \quad (1)$$

A hypothetical number $\alpha^i_a(\max)$ would then obtain if all of product i results from some reaction or reactions in which a is involved. The calculation of $\alpha^i_a(\max)$ for an integral reactor under reasonable assumptions of reaction order, etc., and its use in estimating the fraction of i resulting from the secondary reactions of a will now be carried out and applied.

For an integral reactor of length l, the maximum specific activity at the exit is given by[14]

$$A_i\,(l)(\max) = \int_0^l \frac{(\mathrm{d}V_i/\mathrm{d}x)\,A_a(x)\,\mathrm{d}x}{V_i\,(l)} \quad (2)$$

and the specific activity ratio by

$$\alpha^i_a(\max) = A_i(l)(\max)/A_a(l)$$

where $A_a(x)$ is the activity of the tracer compound at distance x down the catalyst bed, $V_i(l)$ is the total volume of i produced per unit time, and $\mathrm{d}V_i/\mathrm{d}x$ is the rate of formation of i.

Substitution for $A_a(x)$, $\mathrm{d}V_i/\mathrm{d}x$, etc., can be made under various assumptions of reaction orders and rates. Thus $\alpha^i_a(\max)$ can be estimated. The system may be symbolized as follows

$$C_{16}H_{34} \xrightarrow{k_1} a \quad (1)$$

$$a \xrightarrow{k_2} i \quad (2)$$

Assuming that reaction 1 is zero order in hexadecane, that reaction 2 is first order in a, that there is negligible back reaction in both cases, and that the rate of formation of a is much greater than its rate of secondary reaction, $\alpha^i_a(\max)$ may be shown to be given by

$$\alpha^i_a(\max) = \frac{2[V_a(\mathrm{O}) + k_1 l]}{2V_a(\mathrm{O}) + k_1 l} \quad (3)$$

where $V_a(\mathrm{O})$ is the volume of tracer compound, a, injected per unit time and $k_1 l$ is the total volume of a produced by cracking per unit time. In the limiting case when the tracer concentration is insignificant compared to the concentration of a formed by cracking, *i.e.*, for high dilution factors, $\alpha^i_a(\max) =$

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[13] G. Blyholder, *Anal. Chem.*, **32**, 572 (1960).

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

TABLE II

RESULTS OF RADIOACTIVE TRACER EXPERIMENTS NUMBERS 5, 6, AND 7 IN THE CATALYTIC CRACKING OF CETANE AT 372° OVER 37 CC. OF A SILICA–ALUMINA CATALYST

Run 5, 30 min.; gas flows, cc./min.: 0.01 cc. $C_3^*H_6$, 17.0 cc. cetane, 170 cc. helium

Peak no.	Product	Total mmoles	μc. per mmole	Fraction total[a] act.	Sp. act. ratio $\alpha'C_3H_6$
1	Methane	0.064	0.0224	0.0011	0.20
2	Ethylene	.172	.015	.0019	.13
3	Ethane	.127	.0280	.0026	.025
4	Propane	2.734	.1990	.4038	1.75
5	Propylene	3.932	.1140	.3327	1.00
6	Isobutane	7.618	.0184	.1040	0.16
7	1-Butene and isobutylene	2.604	.0133	.0257	.12
8	*n*-Butane	1.299	.0047	.0045	.04
9	*trans*-Butene-2	1.006	.0046	.0034	.04
10	*cis*-Butene-2	0.722	.0157	.0084	.14
11	A pentene	0.217	....	....	..
12	Isopentane	3.083	0.0053	0.0121	0.05
13	1-Pentene	0.496	.016	.0116	.14
14	*n*-Pentane	.482			
15	A pentene	.885	.021	.0138	.18
16	2-Methylpentane	.480	.022	.0079	.19
17	3-Methylpentane	.293	.020	.0044	.18
18	*n*-Hexane and 1-hexene	.180	.020	.0027	.18
19	2,4-Dimethylpentane	.217	.039	.0080	.34
21	An isomeric heptane	.149	.037	.0057	.32
22	An isomeric heptane	.031			
23	2-Methylhexane	.121	.044	.0084	.39
24	3-Methylhexane	.135			
26	*n*-Heptane and 1-heptene	.090	.052	.0035	.46
27	Unresolved dimethylhexanes	.054	.019	.0008	.17
28	Benzene	.059	.080	.0035	.70
29	2,3-Dimethylhexane	.031	.033	.0015	.29
30	3,4-Dimethylhexane	.031			
31	2- and 4-methylheptane	.037	.044	.0027	.39
32	3-Methylheptane	.045			
33	*n*-Octane	.031	.075	.0022	.66
34	Isomeric nonanes unresolved	.008			
35	Toluene	.127	.025	.0024	.22
36	Isomeric nonanes unresolved	.023	.049	.0008	.43
37	Isomeric nonanes unresolved	.015	.049	.0005	.43
38	*n*-Nonane	.015	.080	.0009	.70
39	Isomeric decanes unresolved	.008			
40	*p*- and *m*-xylene	.068	.050	.0028	.44
41	*o*-Xylene	.045	.049	.0016	.43
42	*n*-Decane	.016	.076	.0009	.67
43	*unsym*-Trimethylbenzene	.046	.016	.0005	.14
44	*n*-Undecane	.076	.087	.0049	.76
45	Isomeric C_{11}'s unresolved	.043	.037	.0025	.32
46	Isomeric C_{12}'s unresolved	.045			
47	Isomeric C_{12}'s and C_{13}'s unresolved	.031	.102	.0024	.89
48	*n*-Dodecane	.054	.094	.0038	.82
Coke		2.6% of activity 1.7% of feed			

[a] Excluding radioactivity of coke. [b] Activity summed only through C-5.

2, whereas for a *differential* reactor in which $V_a(O) >> k_1 l$, $\alpha(\max) = 1$.

For consecutive first-order reactions, k_1 assumed to be $>> k_2$, and with the other assumptions above also invoked, $\alpha(\max) = 1.9$ (the value becomes 2.0 if the volume expansion on cracking is included), the crudely determined rate constant k_1 being used.

$\alpha(\max)$ may also be estimated when k_2 is of the same order of magnitude as k_1. This approximates (see below) the observed reaction sequence:

$$C_{16}H_{34} \xrightarrow{k_1} C_3H_6 \xrightarrow{k_2} C_3H_8$$

Here the crude rate data for k_1 and k_2 for successive first-order reactions[15] (under the above approximations) yield the equation

$$\alpha(\max) = \frac{k_1^2(e^{-k_2} - e^{-k_1})(1 - e^{-k_2/k_1})}{k_1(1 - e^{-k_2}) + k_2(e^{-k_1} - 1)} \tag{4}$$

and give an $\alpha(\max)$ value of 1.6. However, this

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(15) S. W. Benson, "The Foundations of Chemical Kinetics." McGraw–Hill Book Co., Inc.. New York, N. Y., 1960, p. 34.

TABLE II (*continued*)

Run 6, 6 min.; gas flows, cc./min.: 0.01 cc. $C_3{}^*H_8$, 16.3 cc. cetane, 170 cc. helium

Total mmoles	μc. per mmole	Fraction total[a,b] act.	Sp. act. ratio[b] $\alpha^{i}{}_{C_3H_8}$
0.012	0.0058	0.0036	0.04
.102			
.067			
1.464	.1560	.7948	1.00
1.762	.0184	.1128	0.12
3.023	.0021	.021	.01
1.022	.0066	.0235	.04
0.548	.0057	.0244	.04
.446			
.236			
.122	....	....	..
1.478	.0025	.0129	.02
0.151	.0023	.0059 +	.01
.209			
.375			
			.01
	.0002		.001

1.3% of activity
3.8% of feed

Run 7, 40 min.; gas flows, cc./min.: 0.01 cc. $C_4{}^*H_{10}$, 16.1 cc. cetane, 170 cc. helium

Total mmoles	μc. per mmole	Fraction total[a] act.	Sp. act. ratio $\alpha^{i}{}_{C_4H_{10}}$
0.072	0.0102	0.0016	0.005
.159			
.134			
2.810	.0009	.0011	.0005
4.622	.0012	.0024	.0006
6.236	.0004	.0011	.0002
1.998	.0009	.0007	.0005
1.185	1.9373	.9664	1
1.039	0.0254	.0173	0.013
0.572			
0.361	....	....	...
2.031	.0024	.0020	.001
0.366	.0027	.0018	.001
.353			
.892			
.585	.0038	.0014	.002
.286			
.206	.0014	.0001	.0007
.286	....	....	...
.201	....	....	...
.080	.0028 .0028	.0004 .0004	.001 .001
.134			
.152			
.101	.0143	.0019	.007
.067			
.088			
.059			
.007			
.038	.0050	.0002	.003
.046			
.034	.0050	.0001	.003
.008			
.101	.0135	.0011	.007
.046			
.026			
.020			
...	....	....	...
.134	.008	.0005	.004
.026			
.013	.0147	.0009	.008
.059			
.072			
...	....	....	...
.020	....	....	...
.025	....	....	...
.033	....	....	...

0.4% of activity
1.5% of feed

is particularly sensitive to the rate constant ratio in this region and the result can only be taken as an indication that α(max) is again a number near 2. The maximum observed value of α(max) in all experiments was 1.8; this was observed for the propylene–propane system.

It is to be remembered that the preceding discussion has been based on the implicit assumption of unit stoichiometry, 1a → 1i; should the reaction under consideration be a polymerization, *n*a→i, α(max) would equal 2*n*. The fraction of i produced by all reactions, a→i, is then α(obs.)/α(max) where α(max) is a number near 2 for our reactor, rate data, unit stoichiometry, and under the assumptions of the preceding paragraphs.

Propylene-1-C^{14} (tracer level 0.06 mole % of hydrocarbon feed).—The data of Tables II, III and IV demonstrate the high reactivity of propylene in secondary reactions. This, coupled with its high concentration in the primary products, indicates

TABLE III

RESULTS OF RADIOACTIVE TRACER EXPERIMENTS NUMBERS 8, 9 AND 10 IN THE CATALYTIC CRACKING OF CETANE AT 372° OVER 37 CC. OF A SILICA–ALUMINA CATALYST

Run 8, 30 min.; gas flows, cc./min.: 0.3 cc. 1-C^{14}-heptene-1, 23.2 cc. cetane, 170 cc. helium

Peak no.	Product	Total mmoles	μc. per mmole	Fraction total[a] act.	Sp. act. ratio $\alpha^{i}_{C_7H_{14}}$
1	Methane	0.080	....	....	..
2	Ethylene	.405	0.0087	0.0085	0.11
3	Ethane	.356			
4	Propane	5.036	.0207	.1336	.25
5	Propylene	6.761	.0169	.1466	.21
6	Isobutane	12.220	.0214	.3355	.26
7	1-Butene and isobutylene	4.710	.0139	.0840	.17
8	*n*-Butane	1.916	.0131	.0554	.16
9	*trans*-Butene-2	1.384			
10	*cis*-Butene-2	0.854	.0162	.0177	.20
11	A pentene	0.356	....	....	..
12	Isopentane	4.039	.0086	.0445	.10
13	Isopentene	0.427	.0116	.0164	.14
14	*n*-Pentane	0.498			
15	A pentene	1.360	.0096	.0173	.12
16	2-Methylpentane	0.694	.0025	.0036	.03
17	3-Methylpentane	.440			
18	*n*-Hexane and 1-hexene	.231	.0098	.0038	.12
19	2,4-Dimethylpentane	.325	.0118	.0049	.14
21	An isomeric heptane	.209	.0145	.0052	.18
22	An isomeric heptane	.068			
23	2-Methylhexane	.151	.1272	.0588	1.56
24	3-Methylhexane	.208			
26	*n*-Heptane and 1-heptene	.102	.0825	.0108	1.00
27	Unresolved dimethylhexanes	.080	.0299	.0031	0.16
28	Benzene	.071	.0553	.0050	.67
29	2,3-Dimethylhexane	.044	.0305	.0022	.37
30	3,4-Dimethylhexane	.012			
31	2- and 4-methylheptane	.044	.0194	.0011	.24
32	3-Methylheptane	.058	.0143	.0011	.17
33	*n*-Octane	.044	.0165	.0009	.20
34	Isomeric nonanes unresolved	.016	.0051	.0001	.06
35	Toluene	.102	.0606	.0079	.73
36	Isomeric nonanes unresolved	.080	.0441	.0045	.53
37	Isomeric nonanes unresolved	.058	.0227	.0017	.28
38	*n*-Nonane	.024	.0166	.0005	.20
39	Isomeric decanes unresolved	.012			
40	*p*- and *m*-xylene	.196	.0390	.0104	.47
41	*o*-Xylene	.071	.0419	.0038	.51
42	*n*-Decane	.035	.0883	.0040	1.07
43	*unsym*-Trimethylbenzene	.058	.0685	.0051	0.83
44	*n*-Undecane	.044	.0382	.0021	0.46
45	Isomeric C_{11}'s unresolved	.011	....	....	..
46	Isomeric C_{12}'s unresolved	.093	....	....	..
47	Isomeric C_{12}'s and C_{13}'s unresolved	.093	....	....	..
48	*n*-Dodecane	.085	....	....	..
Coke		9.4% of activity 2.0% of feed			

[a] Excluding radioactivity of coke.

that these secondary reactions are most important in the determination of the final observed product spectrum. This point of view is substantiated by an examination of the α-values plotted in Fig. 2. In the examination it is to be remembered that *n*-paraffins above C_9 are unresolved from some of their isomers, that *n*-paraffins and α-olefins are unresolved above C_5, and finally that the α-ratios plotted for a given carbon number are averaged over all isomers of the indicated type when they varied from one another by less than 0.1 unit. The values are plotted only to the nearest 0.1 unit for $\alpha \geqslant 0.1$.

For this system α(max) is estimated as already discussed as $1.8 < \alpha(\max) < 2.0$. Thus, significant fractions of all products above C_6 are seen to be formed by reactions of propylene with other compounds or with itself.

The most striking feature of these data is the extremely high α-value of propane demonstrating

TABLE III (*continued*)

Run 9, 30 min.; gas flows, cc./min.: 0.3 cc. 1-C^{14}-heptene-1, 19.0 cc. cetane, 170 cc. helium

Total mmoles	μc. per mmole	Fraction total[a] act.	Sp. act. ratio $\alpha^{i}_{C_7H_{14}}$
0.017	0.003	0.00006	0.02
.309	.011	.0063	.08
.207			
3.112	.032	.1104	.22
4.545	.021	.1059	.15
8.649	.023	.2207	.16
3.495	.021	.0814	.15
1.494	.021	.0613	.15
1.136			
0.713	.025	.0198	.17
0.269	.023	.0069	.16
3.653	.019	.0871	.13
0.479			
0.461	.027	.0138	.19
1.239	.017	.0234	.12
0.833	.021	.0194	.15
.726	.013	.0105	.09
.406	.010	.0045	.07
.382	.017	.0072	.12
.262	.032	.0093	.22
.052	.030	.0017	.21
.138	.266	.1042	1.85
.200			
.114	.144	.0182	1.00
.079	.032	.0028	0.22
.086	.043	.0041	.30
.121	.048	.0069	.33
.009			
.079	.028	.0025	.19
.052	.031	.0018	.32
.052	.063	.0036	.44
.017	.024	.0005	.17
.069	.053	.0041	.37
.052	.052	.0030	.36
.045	.058	.0029	.40
.026	.051	.0015	.35
.009			
.200	.068	.0158	.47
.069	.031	.0024	.22
.026	.063	.0018	.44
.051	.070	.0040	.49
.103	.075	.0086	.52
.045	.080	.0100	.55
.034			
.033			
.045	.122	.0061	.85

6.3% of activity
2.2% of feed

Run 10, 40 min.; gas flows, cc./min.: 0.15 cc. 1-C^{14}-*n*-heptane, 16.6 cc. cetane, 170 cc. helium

Total mmoles	μc. per mmole	Fraction total[a] act.	Sp. act. ratio $\alpha^{i}_{C_7H_{14}}$
0.080	0.0104	0.0039	0.004
.310			
.310	.0073	.0022	.003
3.461	.0010	.0035	.0004
5.757	.0010	.0050	.0004
8.235	.0004	.0034	.0002
3.841	.0010	.0039	.0004
1.601	.0051	.0164	.002
1.711			
0.980	.0022	.0021	.0009
0.358	....	....	...
2.807	.0006	.0016	.0002
0.431	.0024	.0021	.001
0.479			
1.290	.0010	.0012	.0004
0.640	.0032	.0034	.001
.471			
.351	.021	.0072	.009
.398	.0067	.0040	.003
.289	.0027	.0010	.001
.099			
.132	.0088	.0023	.004
.139			
.380	2.482	.9122	1.00
.110			
.058	0.027	.0054	0.011
.030			
.010			
.051	.025	.0024	.010
.051			
.050	.068	.0033	.027
.010	...	....	...
.069	.040	.0027	.016
.030	...	....	...
.020	...	....	...
.040	.023	.0009	.009
.041	...	....	...
.585	.012	.0007	.005
.058	...	....	...
.040	.024	.0082	.010
.179			
.172			
.030	...	....	...
.030	...	....	...
.040	...	....	...
.051	...	....	...

5.4% of activity
1.6% of feed

that some 90 to 100% of the propane is formed through some path involving propylene (90% if $\alpha(\max) = 2.0$, 100% if $\alpha(\max) = 1.8$).

In general the activity of the normal hydrocarbons when radioactive propylene is used as a tracer is greater than that of their branched isomers. The amount of reaction of propylene to benzene is very much higher than its conversion by ordinary alkylation or polymerization to noncyclic hexanes. This ratio of α_{aromatic} to $\alpha_{\text{aliphatic}}$ for C_6-hydrocarbons is to be compared with the same ratio for carbon numbers 7, 8 and 9 where the $\alpha_{\text{aromatic}}/\alpha_{\text{aliphatic}}$ ratio is less than one (carbon numbers 7 and 9) or about equal to one (carbon number 8). Unit stoichiometry has been assumed in the above and all of the succeeding discussion.

Propane-1-C^{14} (tracer level 0.06 mole % of hydrocarbon feed).—Prior to this run most of the radiopropane prepared as described in the Experimental section was unfortunately lost in transfer

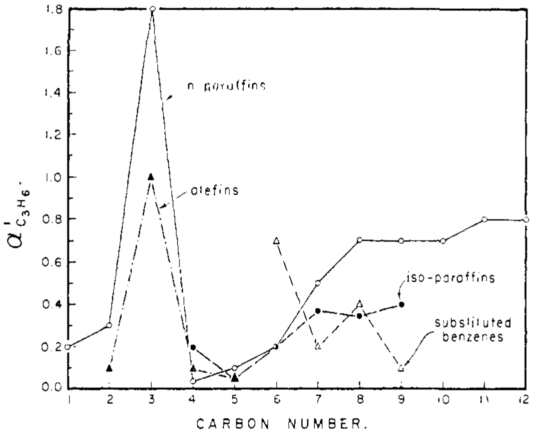

Fig. 2.—Plot of the specific activity ratio $\alpha^{i}_{C_3H_6}$ against carbon number for tracer experiments with radioactive propylene. $\alpha^{i}_{C_3H_6}$ is the ratio of the radioactivities (counts per minute per cc.) of product i at the exit to the radioactivity of the exit propylene.

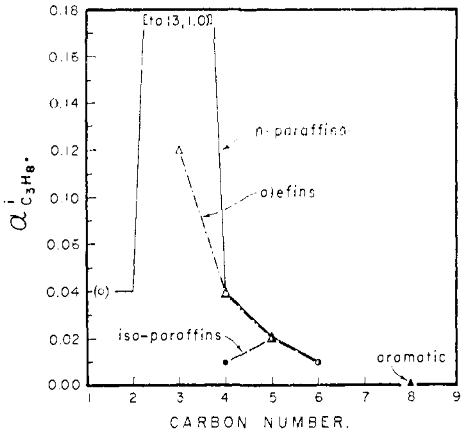

Fig. 3.—Plot of the ratio $\alpha^{i}_{C_3H_8}$ against carbon number (in counts per minute per cc.) for experiments using radioactive propane as tracer.

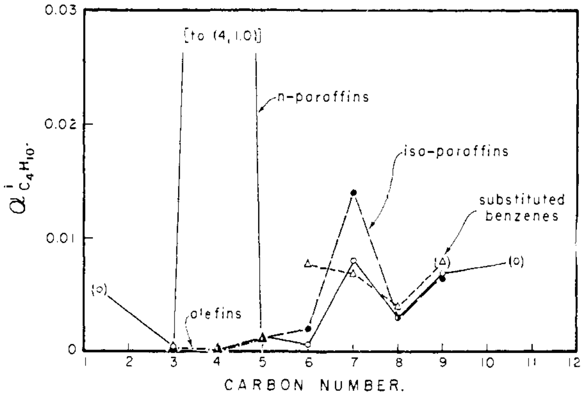

Fig. 4.—Plot of the specific activity ratio $\alpha^{i}_{C_4H_{10}}$ against carbon number for an experiment using radioactive *n*-butane as tracer. Note that points in brackets (for carbon numbers 1, 2, 9, 10 and 11) are averaged.

leaving only enough for a 6-minute run. The amount of product collected was enough for a careful gas-cut analysis, but the liquid cuts were so small as to preclude an accurate and complete radioanalysis although there was enough for several injections allowing spot checks on the activities of several major liquid peaks.

TABLE IV

PERCENTAGE OF ACTIVITY (COKE NEGLECTED) IN VARIOUS PRODUCTS

Run	V	VI[a]	VII	VIII and IX	X
Tracer	C_3H_6	C_3H_8	*n*-C_4H_{10}	1-C_7H_{14}	*n*-C_7H_{16}
Unreacted	33.1	79.5	98.2	1.5[b]	91.2[b]
Dehydrogenated	..	11.3	0.2	..	..
Hydrogenated	40.4	..	..	..	..
Isomers of same carbon number	..	..	0.1	9.6	0.7
Cracked	0.6	0.4	0.5	81.0	5.6
Non-arom. prod. of carbon no. higher than that of tracer	25.3	8.8	1.0	4.8	1.7
Aromatized	0.6	..	<0.1	3.1	0.8

[a] Summed only through carbon number five. [b] *n*-Heptane and 1-heptene were not resolved on the chromatographic column used; hence, this figure is equal to or greater than the unreacted tracer material in these runs.

The α-values plotted in Fig. 3 indicate that propane is quite inert to secondary reaction as compared to propylene. Compared with the data for *n*-butane it is noted, however, that propane undergoes significantly more dehydrogenation. This dehydrogenation is in good agreement with that observed by Andreev.[5,6] Our α-value of 0.12 (372°, cetane in helium) is to be compared with the value 0.08 that we calculate from his data obtained at 500° in the presence of isoöctane (no inert carrier) cracking at very much higher tracer/reactant ratios (13 mole % compared to our 0.06%).

The observed activity of the propylene shows that considerable back reaction exists in the system previously discussed using C_3H_6 as a tracer. This would tend to drop $\alpha^{C_3H_8}_{C_3H_6}$ (max) in Fig. 2 from the value calculated under the assumption of no back reaction. The amount of dehydrogenation is, however, quite small compared to the forward hydrogenation reaction.

Activities in the carbon number 4, 5 and 6 peaks are considerably higher than those found later in the butane and heptane runs, although the lone aromatic checked is somewhat lower. Carbon numbers 1 and 2 were counted as a unit; brackets in the figure indicate this averaging.

n-Butane-1-C^{14} (tracer level 0.06 mole % of hydrocarbon feed).—Specific activity ratios are shown in Fig. 4 and Table II. It will be noted that many peaks ordinarily resolved were counted together in the radioanalysis (in the plot such points are bracketed). This procedure was made necessary by the very low specific activities of all compounds except the added tracer, *n*-butane. In general, then, the statistics were not good and errors in the specific activities may be as high as 20%.

Due to the high dilution of *n*-butane down the bed and the negligible amount of reaction, estimation of $\alpha^{i}_{C_4H_{10}}$ (max) = 2 is very good.

The observation of the very low specific activity of the isobutane peak implies that *n*-butane forms very few carbonium ions (which should easily rearrange to the lower energy *t*-butyl ion and saturate to isobutane) under these conditions, in contrast to relatively extensive carbonium ion formation from olefinic hydrocarbons. The experimental data leading to this conclusion were checked by making a second run under identical conditions. In this run two samples were collected over the first minute of process time and examined for C_4 radioactivity ratios. The results are[16]

		30-min. run	0–30 sec.	50–60 sec.
$\alpha^{i\text{-}C_4H_{10}}_{n\text{-}C_4H_{10}}$	× 10^4	2	3	4
$\alpha^{1\text{-}C_4H_8 \text{ and } i\text{-}C_4H_8}_{n\text{-}C_4H_{10}}$	× 10^4	4	5	3

These isobutane results then substantiate the hypothesis of Greensfelder that the source of the extremely high isobutane/*n*- butane ratio observed in catalytic cracking is the isomerization of higher hydrocarbons followed by cracking. They also corroborate the (non-radioactive) results of Hansford[17] who studied the rate of cracking of pure *n*-butane on silica–alumina and reported a very low rate constant for the reaction butane → isobutane at 482°.

In order to investigate this matter more thoroughly the exchange between tagged butane and isobutane was briefly studied at the elevated temperature of 482°. In this run a mixture of radioactive *n*-butane (0.09 cc./min.) and non-radioactive isobutane (0.22 cc./min.) was carried through the reactor in a stream of helium at 170 cc./min. Two samples were collected; the results are

Sample collected time from start of run	C.p.m./cc. *n*-butane	C.p.m./cc. iso-butane	$\alpha^{i\text{-}C_4H_{10}}_{n\text{-}C_4H_{10}}$	% Conversion[a] / Sec. of contact
0–15 sec.	103,000	132	1.3 × 10^{-3}	0.010
135–155 sec.	106,000	82	0.8 × 10^{-3}	.006
Average			1 × 10^{-3}	.008

[a] Calculated on basis of time of flow through an empty volume of 37 cc., the catalyst volume.

The difference of 110° from 372 to 482° changes the α-value only from 4×10^{-4} to 1×10^{-3}, a factor of roughly two to three, although the two are not strictly comparable since the first was observed in the presence of a stream of cetane. The value of 0.008% conversion/sec. or 0.5%/min. may be compared with Hansford's non-radioactive result of 0.3%/min. (calculated from the limiting slope of his data in a static system, points at 10, 20, 30 and 60 minutes). In view of the disparity of the methods agreement is good.

A final point of interest noted in the inspection of the α-values for the integral reactor results is the relatively greater importance of the alkylation reactions of butane as compared to its isomerization, dehydrogenation and cracking.

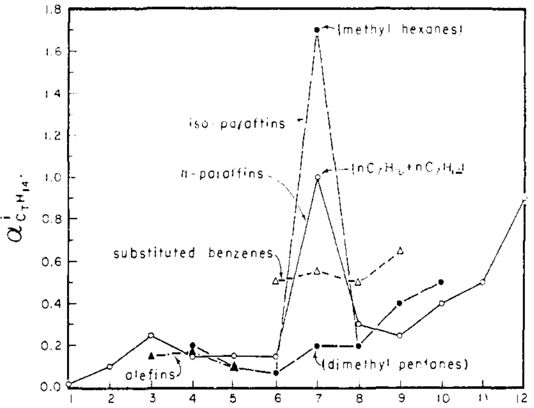

Fig. 5.—Plot of the specific activity ratio $\alpha^{i}_{C_7H_{14}}$ against carbon numbers for an experiment using *n*-heptene-1-C^{14} as tracer.

The extremely low α-values shown in Fig. 4 indicate that the secondary reactions of *n*-butane are of negligible importance in determining the final product distribution.

1-Heptene-1-C^{14} (tracer levels 1.3 and 1.5 mole % of hydrocarbon feed).—Results of two runs differing only slightly in feed rates and tracer levels are found in Table III. The two sets of data can best be compared by examining the $\alpha^{i}_{C_7H_{14}}$ values where agreement is good (within 0.1 unit in most cases) except for *n*-decane where the variation is 0.7 unit. Here the lower value was plotted in Fig. 4 because it more closely fits the general trend exhibited by hydrocarbons in this and all other experiments.

The extreme reactivity of the tracer compound (98.5%) causes a complete breakdown of the assumptions involved in the calculation of α(max). Also, as already mentioned, the *n*-heptane and heptene-1 peaks were chromatographically unresolved. For these two reasons no estimate of α(max) for this system is possible. The ratios plotted in the usual histogram, Fig. 5, have been arbitrarily based on the activity of the heptene–heptane peak and thus indicate only the relative importance of the various secondary reactions. It should be noted that the ratio values (in Fig. 5) are some one to two orders of magnitude greater than these observed for the butane, propane and heptane systems and are directly comparable with those of propylene. Other points of particular interest to be noted in the examination of the data may be listed as: 1. As in the previous experiments, the fraction of alkylation or polymerization products resulting from some reaction of the added tracer compound is significantly greater than the fraction of cracked products from the same source (α alkylation and polymerization > α cracked products).

2. The fraction of methylhexanes resulting from the isomerization of heptene-1 is greater than the fraction of dimethylpentanes from the same

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(16) It may be noted in Fig. 4 that the activities of the butene-2's are arbitrarily set equal to the 1-C_4H_8 and isobutene activity since the butene-2's were eluted from the chromatograph immediately after the *n*-butane peak while 1-butene and isobutene, and isobutane are eluted before *n*-butane. Doubtlessly the tail on the *n*-butane peak (at *ca.* 10^6 c.p.m./cc.) produces an erroneously high count for the 2-butenes even though the amount of *n*-butane included in the cut is very low (<0.1%). Since in all other runs the butenes are in equilibrium with respect to specific activities, the assumption appears plausible. The observed values are found in Table II.

(17) R. C. Hansford, *Ind. Eng. Chem.*, **38**, 849 (1947).

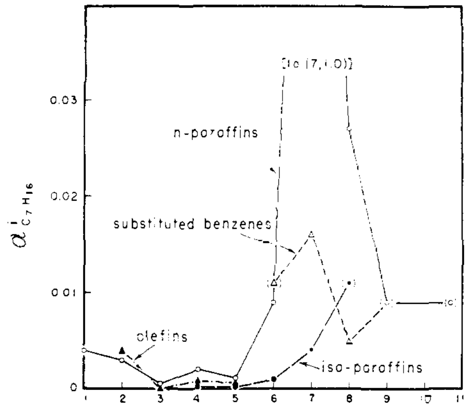

Fig. 6.—Plot of the specific activity ratio $\alpha^{i}_{C_7H_{16}}$ against carbon number for experiments using *n*-heptane-1-C^{14} as tracer.

source α(methylhexanes)/α(dimethylpentanes) = 8.5.

3. The fraction of aromatics from heptene-1 is higher than the fraction of the corresponding aliphatic hydrocarbons (except C-7's) from the same source, by about a factor of 3; but, more important, the α-values for *toluene show no deviation from those for its homologs.* This point alone minimizes the possible importance of a simple dehydrocyclization mechanism in explaining the mode of aromatic formation. However, dehydrocyclization combined with sidechain removal (dealkylation) may be involved in aromatic formation.

4. The extensive amount of reaction observed with this tracer indicates that if it is formed in the primary reaction in any reasonable concentration, it is of great importance in determining the final product distribution. The scheme proposed in the third paper of this series shows a total of 6.2 molecules of C_7H_{14} and 21.7 molecules of $C_7H_{15}^+$ are formed from each 100 $C_{16}H_{34}$ molecules which crack. The reasonable inference is that the reactions of this species are indeed mechanistically important in the determination of the final product distribution.

***n*-Heptane-1-C^{14}** (0.9 mole % of hydrocarbon feed).—Specific activity ratios are shown in Fig. 6. Although the *n*-heptane is chromatographically unresolved from the heptene-1, α for the formation of heptane can be estimated because of the very low dilution factor coupled with the low activity of this tracer compound toward secondary reactions. Because of its low reactivity as well as its low rate of formation from $C_{16}H_{34}$ the *n*-heptane exit concentration is markedly higher here than in control runs. An infrared spectra of the heptene–heptane peak in a control run when compared with standard mixtures resulted in the estimate that some 80 to 90% of this peak is heptane. Assuming the lower value, at most only 7% of the observed tracer plus product peak can be heptene. α(max) then can be estimated from eq. 3 which, assuming that 20% of the control peak is heptene-1 of zero activity, gives

$$\alpha(\max) = \frac{2[V_a(O) + k_1 l]}{2V_a(O) + k_1 l} \times \frac{1}{0.93} = \frac{2(0.15 + 0.06)}{2(0.15) + 0.06} \times \frac{1}{0.93} = 1.3 \quad (5)$$

Contrariwise, assuming that the heptene and heptane activities are of the same order of magnitude, α(max) = 1.2. The values for α now refer to the heptane–heptene peak as reference. The numbers refer to the (average for 30-min. run) observed volume of added tracer and cracked heptane–heptene product at the exit per unit time.

It should be noted that α-values for this heptane experiment are some two orders of magnitude lower than those observed for heptene, once again demonstrating the inertness of paraffinic molecules toward secondary reaction.

Due to the very low specific activities of many products, some peaks usually resolved for radioanalysis had to be counted as a unit. Such averages are indicated by brackets in Table III and Fig. 6.

The ratio of the specific activity of toluene to that of the aliphatic C_7's (other than the tracer heptane) is significantly higher than the xylene to aliphatic C_8 ratio. Since in the case of 1-heptene this preferential formation of toluene was not observed, one can infer that dehydrocyclization is a relatively more important mechanism in the formation from heptane than it is from heptene, compared to other methods of forming toluene. Even so, only a minor fraction of toluene arises from this source. Unfortunately the benzene and the trimethylbenzene peaks could not be resolved from other peaks in large enough amounts to be counted independently due to their low specific activity coupled with the proximity of other peaks. (Chromatographic resolution decreased markedly upon the injection of large samples.)

The relatively high α-value for the *n*-C_8H_{18} is difficult to explain unless the tail of the C_7 influences the C_8 peak. Once again, alkylation reactions are more important than cracking reactions when compared on this "α" basis.

Conclusions

Integral reactor tracer experiments on the secondary reactions of propylene, propane, *n*-butane, *n*-heptene-1 and *n*-heptane during the catalytic cracking of cetane have led to the following conclusions for the respective gases:

1. **Propylene.**—(a) The alkylation, polymerization and hydrogen abstraction reactions of propylene with itself and other compounds are very important in determining the final product distribution. (b) Most ($\geqslant$ 90%) of the propane is formed from propylene. (c) A significant fraction of the aromatics (benzene *ca.* 35%, toluene *ca.* 10%, xylenes *ca.* 20% and *unsym*-trimethylbenzenes *ca.* 5%) are formed in some manner from propylene. The fact that benzene is the most important of these suggests that the aromatization reaction may go directly by way of a two-center condensation from two propylene molecules. However, the dehydrocyclization of higher hydrocarbons followed by dealkylation may also be a factor in aromatic formation. (d) The fraction of any given isomeric or normal hydrocarbon formed in some manner from propylene increases as a rough but direct function of molecular weight in any homologous series. High radioactivity of C_7, C_8, C_9, C_{10}, C_{11} and C_{12} *n*-hydrocarbons suggests

that they are formed in part by the reaction of C_3H_6 with adsorbed olefins or carbonium ions.

2. **Propane.**—(a) Reaction of this species is insignificant in comparison with propylene to products of carbon numbers 4, 5 and 6. (b) The reaction $C_3H_8 \rightarrow C_3H_6$ is the most important reaction of propane investigated. Its rate is low compared with that of the reaction $C_3H_6 \rightarrow C_3H_8$.

3. *n*-**Butane.**—(a) This compound is extremely inert to secondary reaction. (b) At 372° and 482° it does not form appreciable amounts of isobutane. Presumably it does not form appreciable concentrations of surface carbonium ions. (c) Its alkylation reactions are more important than its cracking reactions. (d) It does not dehydrogenate appreciably to the butenes.

4. **Heptene-1.**—(a) It is extremely reactive, the most important reaction being cracking to carbon numbers three and four $\sim$(80%). In order, cracking > isomerization > alkylation plus polymerization > aromatization (Table IV). (b) Monomethyl isomerization is much more important than is dimethyl isomerization. (c) Alkylation by heptyl carbonium ions or polymerization with olefins of lower molecular weights to carbon numbers 10, 11 and 12 is an important factor in their final product mole fractions. (d) It aromatizes but does not aromatize preferentially to toluene as compared to C_6-, C_8- and C_9-aromatics.

5. *n*-**Heptane.**—(a) This compound is extremely unreactive in any given secondary reaction as compared to heptene. (b) In the slight reaction which it does undergo cracking > alkylation plus polymerization > isomerization, aromatization (Table IV). (c) In its aromatization reactions there is a slight specificity to toluene, but the fraction of toluene from this source is only 1% of the total formed.

To sum up briefly, in the catalytic cracking of cetane over silica–alumina catalyst at 375°: (a) The secondary reactions of olefins are much more important than those of paraffins. (b) For any given aliphatic product the fraction formed from secondary (alkylation or polymerization) reactions is directly dependent on and increases with the carbon number. (c) The major fraction of toluene in cetane cracking is not formed by the direct dehydrocyclization of C_7-hydrocarbons. (d) Dehydrocyclization of C_6-hydrocarbons is relatively less important than other reactions in forming benzene. About 35% of the benzene is formed from propylene by some other route than through C_6-aliphatics (benzene activity was much higher than aliphatic activity). The direct polymerization of propylene to benzene and the dehydrocyclization and dealkylation of C_9, C_{10}, C_{11} and C_{12} normal hydrocarbons may well be paths for aromatic formation over cracking catalysts.

Further discussion of the theoretical implications of this paper will be deferred until additional tracer work is completed. The method of using tracers seems capable of giving us eventually a fairly well substantiated theory of catalytic cracking. At the moment it seems best to limit conclusions to the direct inferences that can be drawn and have been outlined above from the group of tracer runs described in this first paper.

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Catalytic Cracking of Hexadecane. II. The Nature of Carbonium Ion-forming Steps and the Exchange of Hydrocarbons with Radioactive Coke[1]

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The ratios of the number of moles of propylene to the number of moles of propane produced and of the radioactivity of the propylene to the radioactivity of the propane were examined as a function of time in differential and integral reactors during the cracking of *n*-hexadecane over a silica–alumina catalyst in the presence of radioactive propylene as a tracer. The rate of coking of the catalyst with *n*-hexadecane and the rate of exchange of carbon between the coke and several hydrocarbons were measured at 372°. The coking rate observations are in general agreement with those previously published. The rate of exchange of carbon from coke with either isoöctane or cetane was very low.

Introduction

It has long been recognized and is generally agreed that the cracking of hydrocarbons over silica–alumina catalysts proceeds through a carbonium ion mechanism. Thus, Tamale, Thomas and Greensfelder[2] suggest that the active sites are composed of truly protonic acids. Interaction of olefins (present in the feed as impurities or formed by residual thermal cracking) with these sites forms the initial carbonium ions which can then react with the hydrocarbon feed molecules, abstracting a hydride ion. The resulting large carbonium ion then proceeds to crack according to general rules originally outlined by Whitmore.[3] Using the example of propylene as the olefin in the cracking of cetane, one may write this mechanism in two separate steps, as

$$C_3H_6 + H^+(\text{cat}) \longrightarrow C_3H_7^+(\text{cat}) \qquad (1a)$$

$$C_3H_7^+(\text{cat}) + C_{16}H_{34} \longrightarrow C_3H_8 + C_{16}H_{33}^+(\text{cat}) \qquad (1b)$$

Greensfelder has shown that the energetics of such a mechanism are consistent with the high energies

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[1] Abstracted in part from the Doctoral thesis of A.V.H.

[2] (a) M. W. Tamele, *Disc. Faraday Soc.*, **8**, 270 (1950); (b) C. L. Thomas, *Ind. Eng. Chem.*, **41**, 2564 (1949); (c) B. S. Greensfelder, H. H. Voge and G. M. Good, *ibid.*, **41**, 2573 (1949).

[3] F. C. Whitmore, *Chem. Eng. News*, **26**, 688 (1948); *J. Am. Chem. Soc.*, **54**, 3274 (1932); **55**, 4153 (1933).