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 ~(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.

Acknowledgments.—This work was supported by the United States Atomic Energy Commission under contract number AT(30-1)-2008. Thanks are also due the Leeds and Northrup Co. which donated the recorder used.

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

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

BY W. ALEXANDER VAN HOOK AND PAUL H. EMMETT

RECEIVED JUNE 29, 1962

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

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

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

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

---

[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).

TABLE I

TOTAL VOLUME (CC. S.T.P.) AND SPECIFIC ACTIVITIES OF PRODUCTS FORMED ON CRACKING CETANE IN THE PRESENCE OF RADIOACTIVE PROPYLENE IN A DIFFERENTIAL REACTOR

90-min. runs at 372°, 17.0 cc./min. (S.T.P.) cetane feed; 170 cc./min., He; apparent time of contact (empty bed), 0.076 sec.

Product	I, control	II, control	III, 0.014 cc./min. of $C_3{}^*H_6$ for 1st 6 min.	IV, 0.014 cc./min. of $C_3{}^*H_6$ for 1st 12 min.	V, thermal run no cat.
Ethylene	0.007	0.008	0.009	0.007	0.006
Ethane	.007	.005	.004	.006	0.004
Propylene	.53	.48	.58	.70	None detected
Propane	.03	.02	.02	.03	None detected
CPM/cc. propylene			96,400	200,000	
CPM/cc. propane			55,000	112,000	

of formation of these carbonium ions.[4] He has also called attention to the fact that in the absence of olefins it is quite possible that the hydrocarbon may react directly with the surface proton according to the reaction

$$H^+(cat) + C_{16}H_{34} \longrightarrow H_2 + C_{16}H_{33}{}^+(cat) \quad (1c)$$

In contrast to this point of view, a second group including Millikan, Mills and Oblad[5] have postulated that the explanation of the acidity of cracking catalysts lies in interfacial octahedrally coördinated alumina which upon the approach of a base (hydrocarbon) shifts to tetrahedral coördination acquiring acidic properties. Thus according to this point of view, no proton need be involved in the active site. For cetane they write the reaction

$$C_{16}H_{34} + \longrightarrow H^-(cat) + C_{16}H_{33}{}^+(cat) \quad (2)$$

In an effort to throw some light on the initial carbonium ion formation we have in differential and in integral reactor tracer experiments compared the amount of the reaction

$$C_3H_6{}^* \longrightarrow C_3H_8{}^* \quad (3)$$

on clean and on carbonium ion contaminated surfaces in the presence of *n*-hexadecane.

We have also measured the rate of coking of a silica–alumina catalyst with *n*-hexadecane and the rate of exchange of the radioactive carbon from a layer of coke with isoöctane or *n*-hexadecane cracked over the catalyst.

Experimental

The integral reactor, tracer addition and sample trapping systems have been previously described as have the techniques of product and specific activity analysis and the specifications of the materials used (see paper I of this series). For exchange experiments and experiments in which the activities of major products were followed as a function of time, the exit of the reactor was fitted with a manually operated switching system so that several samples could be collected in a series of U-traps at −195°. These were then transferred to the chromatograph where the injection facilities had been modified to accommodate them.

The differential reactor used in a short series of experiments was constructed from 10 mm. (i.d.) Pyrex placed in a short tube furnace. A fritted glass disk in the center supported a bed of 20/40 mesh catalyst 3 mm. deep. Two centimeters of broken Pyrex on top of the catalyst served as a preheater. A thermocouple well ran into the center of the reaction tube from the bottom so that the temperature of the gases immediately below the frit was measured. Temperature was kept at 372° with a Thyratron device. Care was taken to keep helium flows and cetane feed rates the same as those used in the integral reactor experiments already described. Products were collected at liquid nitrogen temperature and analyzed by our conventional technique for mole fraction of various products and the specific radioactivity of these same products.

Results and Discussion

Differential Reactor Experiments.—The analytical data obtained for the control and for propylene tracer runs in the differential reactor are summarized in Table I. In the tracer runs, radioactive propylene was added only during the first few minutes of the run; the remaining portion of each reaction period served simply to produce diluents to act as carriers for the radioactive propylene and propane.

The data shown in Table I appear to warrant the following conclusions: 1. The values for the conversion of cetane to propylene per unit volume of catalyst per unit of time are about 3.5 times as great for the integral reactor as for the differential reactor. The statement follows from the fact the 0.53 cc. of propylene was formed in 90 minutes in the differential reactor with a time of contact of 0.08 second, whereas in the integral reactor 90 cc. of propylene was formed in 30 minutes with a time of contact of 12 seconds.

2. The ratio of propane to propylene is much lower in the differential reactor than in the integral reactor. This is, perhaps, to be expected if, as concluded from the tracer experiments in the integral reactor, most of the propane is formed from the propylene rather than being produced directly as a product from the cetane molecule.

In connection with this low propane to propylene ratio, it should be noted that only about 0.025 cc. of propane was formed, on an average, in a 90-minute run, although about 0.7 cc. of cetane vapor cracked.[6] If, in these differential reactor runs, the ratio of higher molecular weight saturated hydrocarbons to propane is similar to that in the integral reactor, it follows that the total amount of saturated hydrocarbons produced in the differential reactor run corresponds to a much smaller number of molecules of saturated hydrocarbons than the number of molecules of cetane cracked. This leads one to suspect that perhaps as much as 0.6 cc. of hydrogen was formed during the cracking of the 0.7 cc. of cetane in the differential reactor. Unfortunately, no analysis was made for hydrogen.

3. According to run 5 of Table I, finite amounts of olefin were detected in the blank thermal cracking run in which no catalyst was used.

---

[4] B. S. Greensfelder, Chapter 27 of "The Chemistry of Petroleum Hydrocarbons," Vol. II, Edited by B. T. Brooks, *et al.*, Reinhold Publishing Corp., New York, N. Y., 1955.

[5] T. H. Millikan, Jr., G. A. Mills and A. G. Oblad, *Disc. Faraday Soc.*, **8**, 279 (1950).

[6] This was estimated from the volume of propylene produced.

4. Using both activity and analytical data, we calculate that in run III 1.9% of the propylene reacts to form propane. This is at the rate of 25.4% reaction per second time of contact. For run IV the corresponding figures are 2.34 and 30.8%, respectively. From the integral run covering a period of 30 minutes the figure is 4.6% per second time of contact. Thus, the rate of reaction of propylene to propane is on the average about 6 times greater per second time of contact in the differential reactor than in the integral reactor. If one corrects for the fact that only one-third of the entering radioactive propylene remained at the end of the integral run, this ratio drops to about 4 for the differential compared to the integral reactor.

In summary, these differential and integral reactor comparisons seem to suggest that the formation of carbonium ions by the reaction of propylene with the surface protons is a step in the formation of propane as suggested by Greensfelder and other workers (eq. 1a and 1b). However, in view of the fact that there do not appear to be enough saturated hydrocarbons formed in the differential runs to account for the observed amount of cetane cracked (0.7 cc. of gaseous cetane) per 90 minute run, it seems very likely that some of the cetane carbonium ions were formed by the reaction with surface protons as indicated by reaction 1c and as suggested originally by Greensfelder.

If reaction 1c occurs in the differential reactor, and if the sum of protons plus $C_nH_{2n+1}^+$ ions on the surface is constant, one would estimate that its rate per surface proton is only a fraction of the rate of reaction 1b per surface $C_nH_{2n+1}^+$ on the surface. This follows from the fact that the over-all rate of cracking per unit time per unit volume of catalyst is only about one-fourth as great in the differential reactor as in the integral reactor and the assumption that the average surface concentration of $C_nH_{2n+1}^+$ ions is higher in the integral reactor due to the enormously greater fraction of cetane cracked. The transformation of radioactive propylene to radioactive propane requires a high surface concentration of protons according to reactions 1a and 1b. The fact that the rate of this transformation of radioactive propylene to radioactive propane is about 4 times as fast in the differential reactor as in the integral reactor is consistent with the catalyst in the differential reactor having a higher ratio of surface protons to surface $C_nH_{2n+1}^+$ carbonium ions than would on an average exist in an integral reactor.

Integral Reactor Short Time Experiments.—In these experiments, a stream of 99.94% hexadecane and 0.06% radioactive propylene in a helium carrier gas was suddenly turned onto the catalyst in the integral reactor. Then, at the exit of the 37-cc. catalyst bed, the product mixture was analyzed for propylene, propane, isobutane and hexadecane as a function of time.

Before carrying out these short-time runs we considered it necessary to make a few preliminary control experiments. These include checking as to whether the integral reactor itself might act as a chromatographic column and thus influence the time at which propylene and propane would first appear at the exit of the reactor. Also, the behavior of propylene by itself and mixtures of radioactive propylene and non-radioactive propane, and of radioactive propylene and nonradioactive isobutane were examined.

To check the importance of a possible chromatographic effect, a Gow-Mac thermal-conductivity cell was substituted for the trap system at the exit of the reactor. With it the retention time of various substances injected at the top of the catalyst bed could be examined as a function of temperature. The standard helium flow rate of 170 cc. per minute was employed and the retention time was determined for air, nitrogen, propane, isobutane and propylene at various temperatures between 200 and 400°. Results were independent of temperature in this range. Air, nitrogen, propane and isobutane took 24 ± 1 seconds to pass through the reactor whereas propylene required 25 ± 1 seconds. We conclude that any chromatographic effect is negligible for these lower hydrocarbons.

Propylene–Propane Mixture.—The passage of 6.9 cc. per minute of non-radioactive propylene through the integral reactor at 372° with 170 cc. of helium per minute showed a small conversion to propane (0.24% reaction to propane per second time of contact). In the presence of cetane at 372°, 4.6% reaction to propane occurred per second time of contact. The partial pressure of propylene at the exit and the over-all space velocities were directly comparable to the long time integral cracking runs.

The rate of the hydrogen transfer between non-radioactive propane and radioactive propylene was checked in the experiment in which a mixture of 6.9 cc. per minute of tagged propylene and 3.4 cc. per minute of propane in 170 cc. per minute of helium were passed through the integral reactor at 372°. These rates approximate the average eluent rates of these substances at the reactor exit during a 30-minute cetane cracking run (paper I). Samples were taken over as short intervals as possible in order to detect any time dependence. The results obtained indicate that the total conversion of propylene to propane is 0.35 ± 0.07% per second time of contact. This compares to the net cracking of non-radioactive propylene as pointed out above of 0.24 ± 0.04% per second time of contact. Hence, the amount of hydrogen transfer to propylene is only 0.10 ± 0.11% per second of contact, and thus within experimental error can be neglected.

Propylene–Isobutane Mixtures.—Similar experiments to those described above were carried out with a mixture of radioactive propylene and non-radioactive isobutane and showed 0.34 ± 0.13% conversion of C_3 to C_4 per second time of contact. The figure obtained for the rate of transformation of propylene by itself to isobutane was 0.33%.

In one final preliminary series of runs a small liquid trap was placed between the reactor and the thermal-conductivity cell. The flow of hexadecane in a helium carrier gas stream was admitted to the reactor and the elution of unreacted cetane fol-

TABLE II

EXIT FLOW AND RADIOACTIVITY OF PROPYLENE, PROPANE AND ISOBUTANE AS A FUNCTION OF TIME DURING THE CRACKING[a] OF CETANE OVER A SILICA–ALUMINA CATALYST

Run	Time interval for sample, sec.	C_3H_8 Cc./sec.	C_3H_8 Sp. act.[b]	C_3H_6 Cc./sec.	C_3H_6 Sp. act.	i-C_4H_{10} Cc./sec.	i-C_4H_{10} Sp. act.
I	10–20	0.00015	11,300	0.0008	60,000	0.0005	500
	20–30	.0011	18,000	.0028	8,600	.0023	4500
	30–40	.0065	11,700	.0053	5,100	.0092	2830
	50–60	.0725	5,640	.0778	1,515	.1245	795
II	10–20	.00048	33,800	.0016	31,900	.0005	1020
	47–52	.049	Sample lost	.048	...	.096	..
	78–80	.061	Sample lost	.068	...	.115	..
	118–120	.055	4,870	.056	2,160	.109	840
III	20–30	.00087	4,950	.0020	2,500	.0022	179
	30–40	.022	1,450	.016	325	.0375	283
	40–50	.063	2,045	.059	535	.110	406
	108–110	.043	2,580	.040	737	.078	170

[a] Twenty cc. of cetane vapor, 0.01 cc. of tagged propylene and 170 cc. of helium was passed per minute into a bed containing 37 cc. of cracking catalyst at 372°. [b] Specific activities are expressed as counts per minute per cc. (S.T.P.).

lowed as a function of time by watching the rate of rise in the liquid trap. Simultaneously, the total gaseous product as a function of time was recorded by the thermal-conductivity apparatus.

The results of this set of runs are shown in Fig. 1 at the three temperatures 291°, 331° and 372°.

The fact that the gaseous products go through a maximum is expected since any cracking catalyst gradually loses its activity during a 30-minute cracking run and is at a maximum at the start of the run.[7] The displacement of the maximum with time as a function of temperature probably reflects the increased physical adsorption of cetane at lower temperatures. It is interesting that the first trace of cetane appears in the liquid trap about the same time at which the maximum in the gas curve is recorded. The ratios of the maxima in the bridge deflection to the steady state are 1.6, 2.0 and 2.2 at 372, 331 and 291°, respectively, although because of possible non-linearity in the (uncalibrated) cell response no quantitative meaning can be attached to these figures.

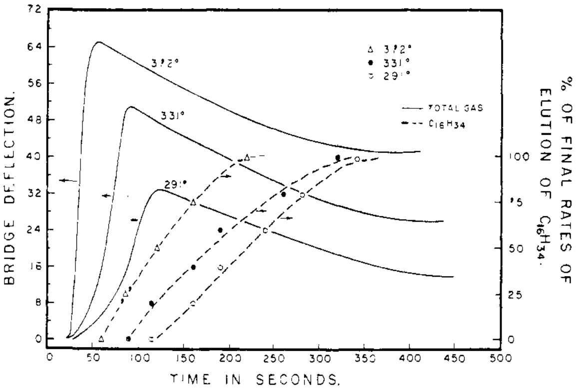

Fig. 1.—Rate of elution of gaseous products and of unreacted cetane as a function of time in an integral reactor containing 37 cc. of silica–alumina cracking catalyst. It should be noted that the bridge deflection is in arbitrary units since the gas composition was not determined.

Final Short Time Runs.—Three separate runs were made to determine the functional dependence of the specific activity ratio of propane to propylene during the first few minutes of cracking in a stream of about 20 cc. per minute of cetane, 170 cc. per minute of helium and 0.01 cc. per minute of tagged propylene. The experimental apparatus and analytical technique have already been described. Due to the extremely small samples collected, the scatter is high.

The analytical data are shown in Table II and plotted for propylene and propane in Fig. 2. As is to be expected, this plot goes through a maximum at the same point at which the total gaseous product as judged by thermal-conductivity goes through its maximum.

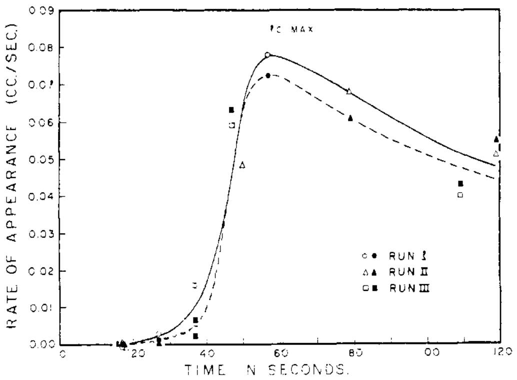

Fig. 2.—Rate of appearance of propylene and propane during the first two minutes of a cracking run with cetane at 372° over a silica-alumina catalyst. The solid line (open points) is for propylene; the dashed line (solid points), for propane.

Although the samples were collected over the indicated time intervals, $t_1 - t_2$, they were plotted at $t_1 + 0.7\ (t_2 - t_1)$ instead of $t_1 + 0.5\ (t_2 - t_1)$. This was done because it was observed that the log (rate of elution) *vs.* time plot was reasonably straight over two orders of magnitude during the first 60 seconds. For a semi-logarithmic function the product is at its average rate at $t = [t_1 + 0.699\ (t_2 - t_1)]$.

The specific activity data are also included in Table II. It should be noted that the scatter is

---

(7) F. H. Blanding, *Ind. Eng. Chem.*, **45**, 1186 (1953).

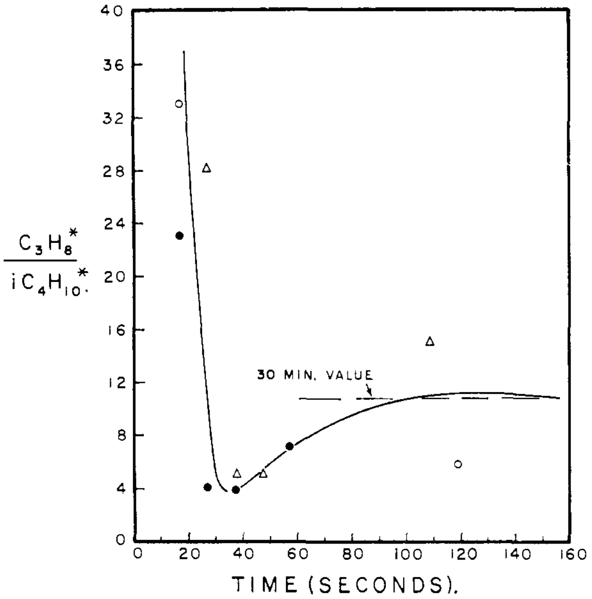

Fig. 3.—Ratio of specific radioactivities of propane to that of isobutane in short time integral cracking runs for cetane over a silica–alumina catalyst.

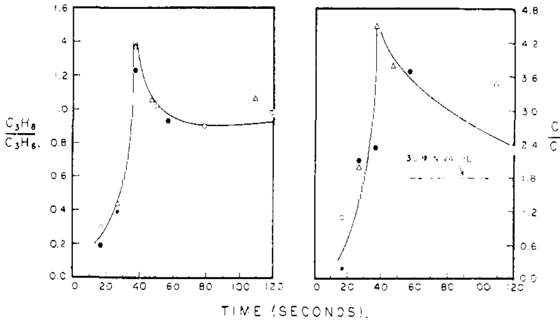

Fig. 4.—Ratios of propylene to propane and of their specific radioactivities in the first 2 minutes of an integral cracking run for cetane over a silica–alumina catalyst. The various symbols indicate separate runs.

bad, chiefly through the necessity of working with very small samples. Also the activities are not reproduced from run to run because of accidental differences in the tracer input rate and the errors in timing during the trapping procedure. In this connection it is to be remembered that the trap-switching system was manually operated.

In order to compare these different runs which were made at slightly different tracer levels, specific activity ratios of propane to isobutane were plotted for each sample. The results are shown in Fig. 3. The ratio of these activities at the start is higher than the integrated equilibrium value by a factor of about 3; it decays through a minimum and then rises to the average for a 30-minute run.

Figure 4 shows plots of the ratio of the rates of appearance of propane and propylene and the ratio of their activities over the first two minutes of reaction. These ratios start well below the equilibrium values in good agreement with the differential experiment described above. They go through a maxima just before the point of maximum conversion as judged by the thermal-conductivity measurements and then decay to the equilibrium values.

The scatter of these results is too great to permit a clear-cut kinetic analysis. However, the following qualitative observations seem warranted: 1. The maximum rate of propylene and propane formation occurs at the end of the first minute. This might be expected on the basis of a slow decrease in the reactivity of any cracking catalyst due to coke formation together with the observation that one minute is the time of appearance of the first cetane in the exit gas (*i.e.*, the time at which the catalyst first attains its equilibrium coverage).

2. Propylene is a primary product; only a fraction of it is converted to propane. The low initial ratio of propane to propylene in the exit gas both in the differential experiments and in these short time integral experiments is in line with this conclusion.

3. The low initial ratio of the specific activity of propane to propylene is also in agreement with the differential reactor experiments.

4. The rapid rise of the ratio of propane to propylene and the ratio of their radioactivities probably both reflect the tendency of the first highly radioactive propylene to adsorb on the fresh catalyst bed. This permits the ratio of the activities of propane to propylene to reach values well above the final steady state ratio of 1.8. These high values of about 4 are reached during the period in which cetane would be sweeping over most of the catalyst and by hydrogen transfer would be removing most of the chemisorbed radioactive propylene by converting it to radioactive propane.

5. The rise in the radioactivity of isobutane to a maximum at about 40 seconds with the resulting diminution in the ratio of the activity of propane to that of isobutane is consistent with an even greater stability of tertiary carbonium ions than propyl carbonium ions. The accumulation of such radioactive carbonium ions would be swept off as radioactive isobutane by the initial wave of cetane through a mechanism of hydrogen transfer.

The differential reactor runs as well as the short time flow experiments in the integral reactor are in agreement with Greensfelder's hypothesis that cetane can react with the surface propyl carbonium ion to form propane and a cetyl carbonium ion on the surface as expressed by reactions 1a and 1b. Indeed, these seem to suggest that with a sufficiently high concentration of propylene and other olefins in the gas phase, reactions such as pictured in 1a and 1b are the principal ones involved in forming surface carbonium ions of the hydrocarbon being cracked. However, the evidence is also strong that in the differential reactor and hence in the first part of an integral reactor, cetane can crack without forming much saturated hydrocarbon. The reaction of surface protons according to reaction 1c is apparently capable of initiating carbonium ion formation of the parent carbonium ion though, as pointed out above at a rate that is only a fraction of the rate of reaction of cetane with $C_nH_{2n+1}^+$ carbonium ions.

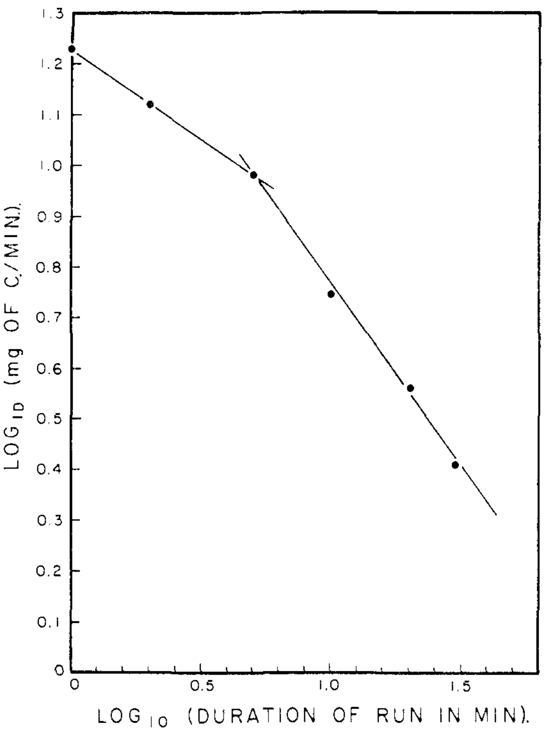

Fig. 5.—Coke formation from cetane cracking in mg. per minute as a function of time.

Coking Experiments.—Prior to making experiments on the exchange of carbon between coke and hydrocarbons that are being cracked, it was necessary to deposit known amounts of coke on the surface of the catalyst. In connection with this deposition a few experiments were carried out on the amount of coke formation from cetane as a function of time. The cetane was passed at a rate of 17 cc. per minute in 170 cc. per minute of helium, at a temperature of 372°. Six runs were made for the duration of 1, 2, 5, 10, 20 and 30 minutes. The experimental technique used in coke determination has already been described in paper I. The data as shown represent the rate of coke formation as a function of time.

The data are well represented on this plot by two straight lines intersecting at five minutes. It is to be remembered that Voorhies[8] found a similar relationship but observed only one straight line. His first point on synthetic catalyst was, however, at fifteen minutes. This author used comparable space velocities 0.3, 0.6 and 1.2 LHSV but the partial pressure of organic reactant was much higher than in the present runs, since he did not employ an inert carrier gas. His investigation was with a Texas gas oil, an extremely complicated mixture, the coking tendency of which would be estimated as much greater than that of normal paraffins. His data show the empirical relationship $C_c = 0.65t^{0.44}$ where C_c is weight percentage of carbon on the catalyst and t is the process period in minutes. Our data yield the empirical relationships $C_c = 0.07t^{0.64}$ from 1 to 5 minutes and $C_c = 0.13t^{0.29}$ from 5 to 30 minutes. Voorhies pointed out that the reaction is most probably diffusion controlled in agreement with its low temperature coefficient. If this is the case, a likely explanation for the observed two intersecting straight lines is an initial rapid coke formation at the pellet surface and pore mouths followed by slower coking on the pore interiors.

Coke Exchange Experiments.—Two separate experiments at different temperatures from different feeds were made. The first experiment was performed using the following procedure: 1. 0.35 cc. of 1.42 mc./mM. $C^{14}{}_3H_6$ was added to a stream of helium flowing over the clean catalyst (372°) at 40 cc./min., over a period of 45 minutes to form the (extremely active) initial coke layer. 2. The temperature was raised to 471° and then swept with helium at 150 cc./min. for 18 hours to remove any adsorbed but uncoked hydrocarbon. 3. The temperature was lowered to 372° and 12 cc. min. (S.T.P.) of isoöctane in 180 cc./min. He injected for 10 min. This step served to dilute the coke activity. 4. The temperature was raised to 448° over a 2.5-hour period while flushing with helium at 180 cc./min., again to remove adsorbed species. 5. Isoöctane was again added under the above conditions this time for 13.5 min. Trapping, analysis and counting were by the standard techniques already described, as was the coke analysis.

Results of this run are shown in Table III for the gaseous products analyzed. Isoöctane was chosen for the reactant in this experiment because of the simple product distribution it gives. Methane and the C_2's were not present in sufficient quantity to be analyzed.

TABLE III

RADIOACTIVITY OF PRODUCTS FORMED ON CRACKING ISOOCTANE AT 372° OVER A SILICA-ALUMINA CATALYST CONTAINING RADIOACTIVE COKE

Substance	C.p.m./mg. of carbon	SA product[a] / SA coke
C_3H_6	223	4.5×10^{-3}
C_3H_8	125	2.5×10^{-3}
i-C_4H_{10}	106	2.2×10^{-3}
n-C_4H_{10}	80	1.6×10^{-3}
Coke	49,300	. . .

[a] Ratio of counts per minute per mg. of carbon in products to counts per minute per mg. carbon in coke. It should be noted that the coke activity here reported was determined at the end of the run (*i.e.*, when at its lowest value).

In a second experiment under the standard conditions of our previous runs, the catalyst was coked as in the first experiment by radioactive propylene at 372° and flushed, again at 372°, with helium at a rate of 125 cc. per minute for 18 hours. This treatment was much milder than that used in the first experiment, and should not disturb the structure of the coke. Cetane was then cracked under the standard conditions used in the integral cracking runs at 372° for 8 minutes. This short process time was used to keep the coke activity reasonably high throughout the entire run. The products in the coke were collected and analyzed in the usual fashion.

The purpose of this experiment was simply to determine if there is significant exchange under our reaction conditions. To this end, it was deemed

---

(8) A. Voorhies, Jr., *Ind. Eng. Chem.*, **37**, 318 (1945).

sufficient to examine only the gaseous products through C_5 as a preliminary measure and then only if these compounds showed a significant activity to proceed with a complete radioanalysis of the higher carbon numbers.

Product ratios and percentage conversions are in agreement with the earlier integral experiments and are not quoted here. The data are collected in Table IV. Again note that the coke activity was measured at the end of the cracking run.

TABLE IV

RADIOACTIVITY OF PRODUCTS FORMED ON CRACKING CETANE AT 372° OVER A SILICA–ALUMINA CATALYST CONTAINING RADIOACTIVE COKE

Substance	C.p.m./ mg. carbon	Total, cc.	Total counts	$\frac{\text{SA product}}{\text{SA coke}}$
CH_4				
C_2H_4	18	1.3	24	1.8×10^{-3}
C_2H_6				
C_3H_8	9	14.8	222	0.9×10^{-3}
C_3H_6	10	11.2	179	1.0×10^{-3}
i-C_4H_{10}	14	26.8	778	1.4×10^{-3}
i-C_4H_8 1-C_4H_8	9	6.4	128	0.8×10^{-3}
n-C_4H_{10}				
cis + *trans*-C_4H_8	7	8.6	120	0.7×10^{-3}
Pentanes and pentenes	2	9.6	58	0.2×10^{-3}
Coke	10,200	54 (mg.)	550,000	1

The results of this experiment clearly indicate that coke exchange plays a negligible role in determining the activity spectrum of our previous results. Still the fact that about 0.5% of the total activity of the coke plus that of the gaseous product activity is found in these products is surprising and perhaps significant. Incidentally, it might be remarked that from the fact that the propane radioactivity is no higher than that of the other hydrocarbons one has fair assurance that the radioactivity transferred to the gas phase is not due to a hydrogen transfer to residual chemisorbed propylene that might have been left from the coking step itself.

One final way of summarizing coking formation that actually took place during the regular tracer experiments in the integral runs given in paper I is to summarize the ratio of the percentage of the total radioactivity in the coke divided by the percentage of the feed gas converted to coke. These ratios were found to be 1.5, 0.3, 0.3, 3.8 and 3.4 for the runs using radioactive propylene, radioactive propane, radioactive normal butane, radioactive heptene-1 and radioactive normal heptane, respectively. It is easy to understand why the ratio for propylene and heptene-1 are both much greater than the ratios for propane and normal butane because in general olefins are more prone to form coke than are the saturated hydrocarbons. However, it is difficult to understand why the ratio is so high for normal heptane. The answer to this latter observation will have to wait further experimental work.

Acknowledgments.—Thanks are due to the Atomic Energy Commission for supporting this work under contract No. AT 301-2008, and to the Leeds & Northrup Co. for the donation of two recorders used throughout the work.

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY, SCHENECTADY, NEW YORK]

The Kinetics of Propane Cracking on Nickel[1]

BY DOUGLAS W. MCKEE

RECEIVED MAY 23, 1962

The catalytic cracking of propane on unsupported nickel has been studied over the temperature range 100–200°. Methane, small amounts of ethane and a carbonaceous surface residue of variable composition were the products of the reaction, which proceeded with an activation energy of 15 ± 1 kcal./mole. A zero-order dependence of the rate of reaction on the partial pressure of propane was generally found, although poisoning of the catalyst by strongly adsorbed residues became increasingly important at higher temperatures. Possible mechanisms of the cracking reaction are discussed.

Introduction

Comparatively little information is available concerning the chemisorption and dissociation of saturated hydrocarbons on metal surfaces. Thus, in spite of the fact that the subject of hydrocarbon cracking on silica–alumina and oxide materials has a very considerable literature and the reactions and intermediates involved are fairly well understood, few detailed studies have been made with metallic catalysts and the mechanism of carbon–carbon cleavage on metal surfaces is not well defined. Most of the studies which have been made, such as those of Morikawa, Trenner and Taylor,[2a] are concerned mainly with hydrocracking, in which both hydrocarbon and hydrogen are present in the gas phase. The situation here is probably different from that which occurs when the hydrocarbon is present alone. A recent study from this Laboratory[2b] has shown that the C–H bonds in ethylene can be broken at as low as −78° on a nickel catalyst, whereas C–C bond cleavage did not become appreciable until 80°. In the case of ethylene the deposition of involatile carbonaceous residues on the surface during the course of the reaction seemed to play an important role in the activity of the metal. As a continuation of this work, it was decided to compare the behavior of

---

[1] This work was made possible by the support of the Advanced Research Projects Agency (Order No. 247-61) through the United States Army Engineer Research and Development Laboratories under Contract Number DA-44-009-ENG-4853.

[2] (a) K. Morikawa, N. R. Trenner and H. S. Taylor, *J. Am. Chem. Soc.*, **59**, 1103 (1937); (b) D. W. McKee, *Nature*, **192**, 654 (1961); *J. Am. Chem. Soc.*, **84**, 1109 (1962).