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The Influence of Added-Back Water Vapor on the Chemisorption and on the Rate of Catalytic Cracking of Paraffins on a Silica-Alumina Catalyst*

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The effects of added-back water on the cracking and isomerization of 2,2,3-trimethylbutane (triptane) were studied at 162°, 180°, and 200°C; on 2-methylpentane, at 100°C; and on *n*-heptane, at 200°, 250°, and 300°C. The optimum amounts of added-back water were in the range 0.05% to 0.15%; the increase in the rates of cracking at the optimum amounts was usually about fivefold. For the isomerization of 2-methylpentane it was about 22-fold. The radiotracer adsorption experiments with *n*-heptane-1-^{14}C at 10 mm Hg and 110°C confirmed three types of chemisorption, namely, instantaneously exchangeable chemisorption (Type 1), slowly exchangeable chemisorption (Type 2), and nonexchangeable chemisorption. The amounts of nonexchangeable chemisorption (V_{NE}), Type 2 chemisorption (V_2), and total chemisorption ($V_1 + V_2 + V_{NE}$) were observed to decrease upon addition of water but the amount of Type 1 chemisorption (V_1) increased. The Type 1 chemisorption is apparently weaker than Type 2 and some portion of it may be removed during evacuation. The correlation between the influence of added-back water on the cracking of *n*-heptane and on the amount of Type 1 chemisorption is only qualitative; the relative increase in the amount of this chemisorption upon addition of water is somewhat smaller than the relative increase in the cracking rate. Accordingly, one must conclude that the marked enhancement of catalytic cracking and isomerization rates caused by added-back water is not yet completely explained.

INTRODUCTION

The effects of added-back water and the degree of dehydration on catalytic cracking (*1–3*), catalytic isomerization (*3–6*), and rate of exchange (*4, 6–12*) of the hydrogen of hydrocarbons with deuterium on deuterated silica-alumina catalysts have been studied by many investigators. In all of these reactions the adding back of a few tenths of a percent of water vapor has been found to have a pronounced accelerating effect on the reaction rate. In an effort to explain the influence of added-back water, MacIver, Emmett, and Frank (*13, 14*) employed a radiotracer technique for the measurement of isobutane chemisorption on a silica-alumina catalyst. They found a reversible chemisorption of about 0.003 cc/g and an irreversible or nonexchangeable chemisorption of about 0.001 cc/g. However, they did not observe any appreciable increase in the amount of reversible or total chemisorption as the amount of added-back water was increased.

Larson and Hall (*15*) repeated the study of isobutane chemisorption using a circulating system so built that the equilibrium "adsorption–desorption" rates could be measured. They found two kinds of reversible chemisorption, namely a weak chemisorption (Type 1), and a strong chemisorption (Type 2); they found also a nonexchangeable (NE) chemisorption. The Type 1 chemisorption could be removed by adding nonradio-

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* Based on the Ph.D. thesis of K. Matsushita, The Johns Hopkins University, 1966.

active isobutane. Type 1 and the nonexchangeable chemisorption were independent of the pretreatment of the catalyst and were not materially influenced by added-back water vapor. The latter, however, caused a decrease rather than an increase in the amount of exchangeable chemisorption (Type 2), as well as in the mass transport rate, $R(2)$, of the exchange between chemisorbed radioactive isobutane and gaseous nonradioactive isobutane. Moreover, from the experimental observation of markedly increased rates of hydrogen exchange between gaseous nonradioactive iso-C_4D_{10} and the catalyst, they concluded that an additional process for hydrogen exchange became important when water was added back.

From the tracer experiments on isobutane and the cracking of some of the other hydrocarbons it appeared that added-back water vapor has a much larger influence on cracking than on chemisorption of the hydrocarbon. However, to confirm this conclusion it seemed desirable to ascertain the effect of water vapor on the cracking and chemisorption of one and the same hydrocarbon. To this end, the present work on the chemisorption and cracking of *n*-heptane was undertaken. Tracer work had originally been planned for triptane and for 2-methylpentane. The influence of water vapor on the cracking and the isomerization of these hydrocarbons was determined but the chemisorption studies were not done due to our inability to find a supplier of either radioactive triptane or radioactive 2-methylpentane.

EXPERIMENTAL

Apparatus. The apparatus consisted mainly of four parts: a purification train and gas volume measuring system, a static system for catalytic activity tests, a circulating system for catalytic activity tests, and a radiotracer adsorption system. The hydrocarbon purification train was constructed of a series of traps containing glass beads, sodium hydride, and silica-alumina which was pretreated with oxygen and was evacuated under a high vacuum at 500°C. The volume measurement system was a standard type. The static system for catalytic activity tests was constructed of capillary glass tubing and a catalyst sample tube which contained a thermocouple well, a manometer, and two coolant traps, one on each side of the catalyst tube. The circulating system for catalytic activity tests was constructed of 6-mm o.d. glass tubing and consisted of a circulating pump and a catalyst sample tube with a preheating spiral at the bottom and a thermocouple well at the top. The gas circulating pump was similar in design to that described by Kallo and Schay (*16*), and by Kallo, Preszler, and Payer (*17*), and was double-acting and completely enclosed in the system.

The radiotracer adsorption system was similar in design to that of MacIver *et al.* (*13, 14*) and that of Larson and Hall (*15*). The details of this part of the apparatus are illustrated in Fig. 1. The circulating pump was the same one described above and the catalyst tube was the same as the one used for the circulating system for catalytic activity tests. All of the mercury cutoffs in the system were designed so as to operate not only at low pressure but also at higher pressure. A Kummer-type Geiger tube (*18*) was built into the system so that the radioactivity could be measured at any moment while the gas mixture was circulating. It involved a Tracerlab Geiger tube (7G-12) separated by a thin mica window (3–4 mg/cm^2) from a 5-cc chamber through which the gas could be circulated.

Catalysts. A batch of 20- to 35-mesh Davison Chemical "Code 980" catalyst was used in the investigation; it was prepared by sieving crushed pellets from the same supply from which Van Hook and Emmett (*19, 20*), and Hightower and Emmett (*21, 22*) obtained their samples. Following the normal pretreatment, the surface area determined by the standard BET nitrogen adsorption technique was about 360 m^2/g. The composition of the catalyst was reported to be as follows: 13.21% Al_2O_3, 0.03% Fe, 0.30% SO_4^{2-}, 0.02% Na_2O, and 86.44% silica, by difference.

Gases. 2,2,3-Trimethylbutane (triptane) was purified prior to storage by passage through the purification train described earlier. The final purity was at least 99.9%, and no olefins were detected. 2-Methyl-

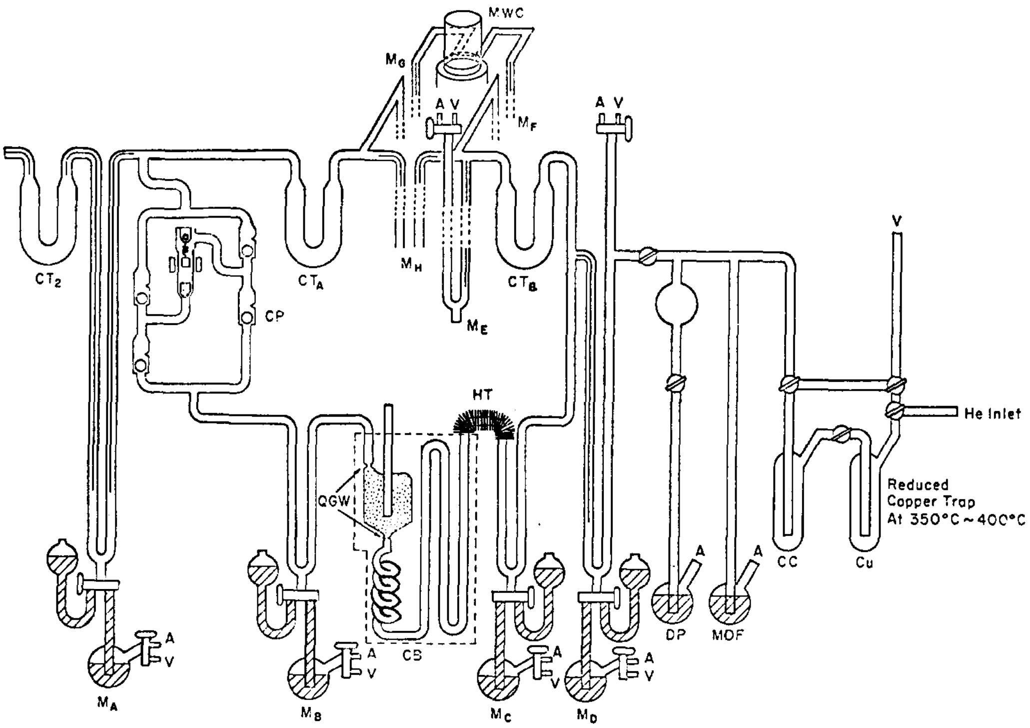

FIG. 1. The radiotracer adsorption system. The abbreviations are as follows: CT, coolant traps; M_{A-H}, mercury cut-offs; A, air pressure, V, vacuum; CP, circulating pump; CB, catalyst bed; QGW, quartz glass wool; HT, heating tape; MWC, mica window chamber; DP dibutyl phthalate; MOF, mercury overflow; CC, charcoal trap; and Cu, copper trap (reduced copper at ~350–400°C).

pentane was purchased from Matheson, Coleman, and Bell Corp., and was designated as 99.99 mole % "criterio-quality" reagent,# AA8476. It was not further purified prior to storage except for being degassed by repeated cycles of evacuation with freezing and melting. *n*-Heptane was purified in the same manner as triptane. Gas chromatographic analyses showed no impurity except 0.01% methylcyclohexane.

n-Heptane-1-^{14}C was purchased from Nuclear Research Chemicals, Inc., Orlando Florida. The specific activity was 0.07145 millicuries/mmole. The radiochemical purity was 97.8% before purification. After contact with dehydrated silica-alumina catalyst at room temperature for 4 to 5 hr, the heptane showed a radiochemical analysis of 99.11% *n*-heptane, 0.77% in the range between C_1 and C_6, and no more than 0.12% heptenes. The portion designated as heptenes may actually have been due to the long tail of the *n*-heptane on the chromatograph. This seems to be the case since an activity was observed over the range between *n*-heptane and 1-heptene comparable to the total activity designated as "heptenes." Flame conductivity gas chromatographic analysis revealed no heptene.

Tank helium was carefully purified through a trap of reduced copper operated at 350° to 400°C and a trap filled with activated charcoal and kept at liquid nitrogen temperature.

The distilled water used in the present investigation was deaerated by repeated cycles of freezing at −78°C, evacuation, and melting.

Procedure for cracking and isomerization experiments. For the cracking of triptane and the isomerization of 2-methylpentane 6.037 g of catalyst was used. The same catalyst was used repeatedly for both studies; also, the same treatment with an oxygen flow of 80 to 100 cc NTP/min for 6 hr at 500°C and subsequent evacuation under

10^{-6} mm Hg/for 10 hr at 515–525°C was employed. A static system was used for these experiments; the dead volume was 26.32 cc. The amount of reactant for each series was the same and was sufficient to produce approximately 50 mm Hg initial pressure with the catalyst at the operating temperature.

In each run the amounts of reactant and water were volumetrically measured. A known amount of water vapor was added each time at the reaction temperature after the catalyst treatment but before introduction of the reactant, throughout the present investigations. The reactant was introduced to the system while the catalyst was kept at the predetermined reaction temperature. The pressure of the system was read during the reaction. At the end of a 60-min reaction period, the gas mixture was trapped by cooling a sidearm with liquid nitrogen for 10 min and then was transferred to a sample storage bulb. The analyses of the gas mixture were made on a Vapor Fractometer with a flame-ionization detector (Perkin-Elmer V.F., model 154C). The column used for the gas analyses of triptane cracking products was a Golay capillary columne (349R) which was coated with polypropylene glycol (PPG) and operated at room temperature. This is specified as Product Analysis 1 or PA_1. A Golay capillary column (377U) which was coated with squalane was employed and operated also at room temperature for the analyses of 2-methylpentane isomerization products. This is designated as PA_2.

For the cracking of *n*-heptane a circulating system was employed. The dead volume of the system was about 104 cc and the amount of catalyst was 5.221 g. The amount of reactant introduced was sufficient to produce an initial pressure of about 30 mm Hg. After the introduction of the reactant which was frozen in a trap by liquid nitrogen, prepurified helium was introduced to fill the system up to 1 atm. When the reactant trap had warmed to room temperature, the circulating pump was switched on and the counting of the time of reaction was begun. The speed of circulation was adjusted at 0.5 liter/min. About 0.25 cc of gas mixture was taken several times from the system by a hypodermic syringe for analyses of gas composition during the reaction. The gas analyses were made by two gas chromatographic units: Perkin-Elmer Vapor Fractometer (model 154C) and Aerograph HY-FI (model 600). Both units had flame-ionization detectors. The Perkin-Elmer V.F. made use of a Golay 377U capillary column, and an operating temperature of 38°C. This is designated at PA_3. The conditions used for Aerograph were 2 m of $\frac{1}{8}$-inch alumina-packed column and a temperature of 150°C. This is designated as PA_4. At the end of a 60-min reaction a liquid nitrogen trap was placed on a U tube for 10 min while the gas mixture was kept circulating. The trapped hydrocarbons were transferred to a sampling flask and the gas mixture was analyzed after dilution with helium.

Procedure for studying the chemisorption of radioactive heptane. For the study of the chemisorption of *n*-heptane-1-^{14}C by radiotracer technique, the same 5.221 g of catalyst used for *n*-heptane cracking reaction was employed. The volumes of the entire system and the mica window chamber were about 200 cc and 11 cc, respectively. When 1 cc STP of the radioactive heptane was admitted to the adsorption system (without the catalyst being present), the counter registered 1.3686×10^4 counts/min. The background was counted before and after each run for at least 30 min.

In general, three steps were involved in the radiotracer technique for measurement of *n*-heptane chemisorption. These were chemisorption of *n*-heptane-1-^{14}C, measurements of the reversible adsorptions, and measurement of the irreversible adsorption. These are described separately below.

Chemisorption of n-heptane-1-^{14}C (Step 1). The catalyst which was employed previously for the study of *n*-heptane cracking was used again after it was treated with a stream of oxygen at 525°C and degassed under a high vacuum at 535°C. The catalyst was brought to the predetermined temperature, namely 110°C, and a known amount of water was added. Then about 7.35 cc STP of the radioactive compound (the amount needed to make a pressure of 10 mm Hg at 110°C) was measured volumetrically and introduced into the system by cooling CT_A (see Fig. 1) with liquid nitrogen. The radioactive compound, after being diluted with prepurified helium up to 1 atm, was circulated over the catalyst for either 60 min or 180 min. The speed of circulating the gas mixture was set at approximately 500 cc NTP/min. The temperature was maintained within ± 0.5°C by a Thyratron regulator. At the end of a preset duration of chemisorption, a liquid nitrogen bath was placed on the trap (CT_A) for 60 min while the gas mixture was kept circulating. After the physical adsorption was trapped by the circulation of the gas mixture through the trap (CT_A) while the catalyst was kept at 110°C, helium was evacuated through trap CT_2 cooled by liquid nitrogen. After the transfer of the radioactive *n*-heptane from the system to a sampling vessel the system was thoroughly evacuated for 9 hr under high vacuum while the catalyst was kept at 110°C. In some cases the catalyst was cooled down to 79°C for removing the physical adsorption. The *n*-heptane-1-^{14}C which was left on the surface after 9-hr evacuation at 110°C was considered to be chemisorbed. The amount left on after evacuation at 79° is called "chemisorption," though admittedly it may have included some physical adsorption.

Measurement of the reversible adsorption (Step 2). Approximately 8 cc STP of nonradioactive *n*-heptane was measured volumetrically and introduced into the system, together with enough helium to raise the pressure to 1 atm. The gas mixture was then circulated. At the same time, the counting was initiated both by scaler readings and by recording the output of the rate meter on a chart. The temperature of the catalyst was maintained at 110°C from the beginning of this exchange process. It was observed that approximately 12 hr were necessary to determine the reversible portion of chemisorption by the exchange method. After a 12-hr exchange reaction between adsorbed radioactive and gaseous nonradioactive *n*-heptane, a liquid nitrogen bath was placed at the trap CT_A for 1 hr while the gas mixture was circulated and the catalyst was maintained at 110°C. Then, helium was evacuated and the condensed heptane was transferred to a storage bulb. The system was then evacuated at 110°C for 2 hr under a high vacuum.

Measurement of the irreversible adsorption (Step 3). Following Step 2, the system was filled with oxygen up to 1 atm. The reactor temperature was brought up to 535°C and the gas was circulated. After the catalyst was treated with oxygen at 535°C for at least 2 hr, an acetone–Dry Ice bath was placed on the trap CT_A. This combustion process was continued for more than 8 hr at 535°C. Oxygen was evacuated through the trap CT_2 cooled with liquid nitrogen until the pressure became 10^{-3}–10^{-4} torr. After about 30-min evacuation, carbon dioxide from trap CT_2 was transferred back to the system and the latter was filled with helium. The gas mixture was then circulated through the counter. When the recording of the ratemeter output became stabilized, a 20- to 30-min reading of the superscaler was made to obtain the average counting rate and, hence, the amount of irreversible adsorption.

Treatment of the data obtained in the study of the exchange process. (1) The "integral average counting rate" was defined as the counting rate obtained by dividing the total counting recorded in the Tracerlab Superscaler by the time from the beginning of the circulation. This indicates a relative exchange behavior as a function of the catalyst treatment. (2) Rate meter average counting rate was defined by dividing the difference of the counting recorded in the Tracerlab Superscaler at time t_1 and t_2 by $t_2 - t_1$. This is the same principle as the reading of the output of the ratemeter. Therefore, this gives the amount of radioactive hydrocarbon present in the circulating system at a given time. (3) The amount of the exchangeable chemisorption (V_E) was determined by multiplying the average counting rate after the 12-hr exchange process by $V_{n\text{-}C_7}/(V_{n\text{-}C_7}-5)$, where $V_{n\text{-}C_7}$, is the volume of nonradioactive *n*-heptane introduced. The factor, $V_{n\text{-}C_7}/(V_{n\text{-}C_7}-5)$ takes account of the fact that about 5 cc STP of *n*-heptane is physically adsorbed at 110°C and at 10 mm Hg and the average counting rate measured is only from the gas-phase *n*-heptane-1-^{14}C, which is approximately $V_{n\text{-}C_7}-5$. It was also assumed that the radioactive compound is distributed homogeneously in both the gas phase and the physically adsorbed phase. The amount of the "instantaneously exchangeable" (Type 1) chemisorption (V_1), was determined by extrapolating the plots of the rate meter average counting rate against time to zero time. The amount of the "slowly exchangeable" (Type 2) chemisorption (V_2) was determined as $V_E - V_1$. (4) Kinetic treatment of the data was carried out by applying the theory developed by Duffield and Calvin (*23*), Marcus (*24*), and Winter (*25*), and applied by Cheselske, Wallace, and Hall (*26*), and Larson and Hall (*15*). The transport rate constant k for *n*-heptane at 110°C and at 10 mm Hg, was taken as 2.303 times the slope of the plots of log $(C_\infty/C_\infty - C]$ versus time of exchange. The k thus obtained is the probability of desorption, i.e., the rate constant per molecule for transport into the gas phase (*15*). The mass transport rate R is calculated by assuming $^{14}N_0 \ll {}^{12}N_0$ in the equation

$$k_i \equiv R_i \frac{^{14}N_0 + {}^{12}N_0}{^{14}N_0{}^{12}N_0}$$

Thus, $R_i \approx k_i{}^{14}N_0 \propto k_i{}^{14}N_0(i)$, where i = 1 or 2.

EXPERIMENTAL RESULTS

Catalytic Activity Tests

The experimental results for each compound will be presented here and discussed separately.

2,2,3-Trimethylbutane (Triptane). Table 1 shows typical product distributions for two runs. The effect of water on the reactions of triptane is shown in Table 2 and Fig. 2.

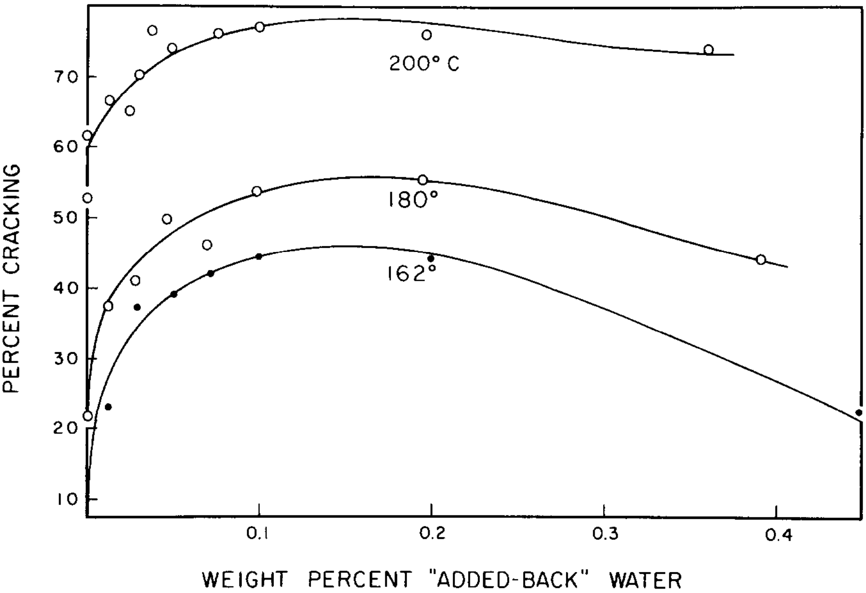

FIG. 2. Percent cracking of triptane at 162°, 180°, and 200°C as a function of the amount of added-back water.

Olefinic products were present in only insignificant amounts for the study of the effect of water on the cracking.[1] The optimum amount of added-back water was in the range between 0.1 and 0.2 wt % at all three temperatures studied. The lower the reaction temperature, the more significant the effect of added-back water on catalytic cracking activity.

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[1] This is understandable since the usual small amount of olefins could have been adsorbed or converted to paraffins by hydride ion transfer in the 1-hr time of contact in the static system.

TABLE 1

Typical Product Distributions from the Catalytic Cracking of Triptane[a]

Added-back water (wt %)	Hydrocarbon[b]	Mole fraction (MC_k)	% Conv. to each product[c]	Total % conv.
0	$C_3(+C_3^{2-})$	0.1002	—	—
	iso-C_4	0.3206	35.63	—
	iso-C_5	0.1091	12.13	52.83 (C)
	2,3-Me_2C_4	0.0326	3.63	—
	3-MeC_5 (2-MeC_5)	0.0129	1.44	—
	2,4-Me_2C_5	0.0168	1.87	—
	2-MeC_6	0.0219	2.43	—
	2,3-Me_2C_5	0.008	0.88	6.99 (I) (14.8 II)
	3-MeC_6	0.0162	1.80	—
	2,2,3-Me_3C_4	0.3617	40.19	—
0.10048	$C_3(+C_3^{2-})$	0.1497	—	—
	iso-C_4	0.4776	56.17	—
	iso-C_5	0.1366	16.06	77.23 (C)
	2,3-Me_2C_4	0.0291	3.42	—
	3-MeC_5	0.0134	1.58	—
	2,4-Me_2C_5	0.0111	1.30	—
	2-MeC_6	0.0150	1.77	5.17 (I) (22.3 II)
	2,3-Me_2C_5	0.0057	0.67	—
	3-MeC_6	0.0122	1.43	—
	2,2,3-Me_3C_4	0.1496	17.60	—

[a] Initial pressure, 50 mm Hg; temp., 200°C; reaction time, 60 min; 6.037 g catalyst.

[b] No appreciable amount of olefins was detected except some small amount of propylene. C_1 and C_2 products were also negligible.

[c] Percent conversion for cracking (C) is defined by $100(x)\ MC_k/\Sigma_{j=4}^{j=7} MC_j$; k may have values of 4, 5, or 6. The total cracking figure is the sum of these terms for $k = 4$, 5, and 6. Percent isomerization (I) is calculated with $k = 7$, omitting, of course, the mole fraction of triptane. In parentheses are shown the values for isomerization on the basis of the ratio of the mole fractions of the various C_7 isomers to the total C_7's including triptane. These two methods of calculations will be designated as Methods I and II, respectively, for calculating the percent isomerization.

As can be seen in Table 1, the percent isomerization as calculated (footnote *c*, Table 1) by the final C_7 isomers divided by the initial triptane is rather meaningless because of the extensive decomposition of all the C_7 molecules. Probably a better calculation is the one based on the analysis of all of the C_7 species at the end of the run. Such a calculation is shown in the last column of Table 2 and in parentheses in the last column of Table 1. These latter calculated values for isomerization are shown in Fig. 3.

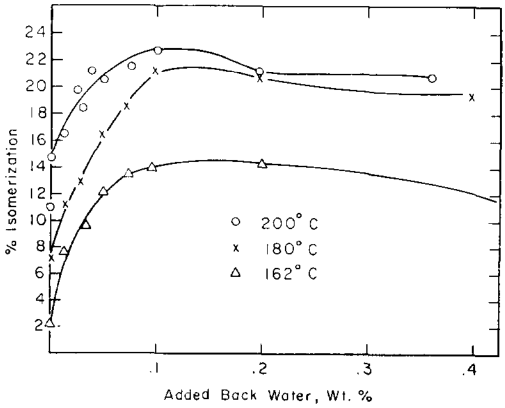

Fig. 3. Percent isomerization of triptane at 162°, 180°, and 200°C as a function of the amount of added-back water. See Table 2.

The total pressure of the system during the cracking reaction of triptane is plotted in Fig. 4. The most significant observation made in the figure is the decrease in the

TABLE 2
PERCENT CONVERSION OF TRIPTANE UNDER VARIOUS CONDITIONS[a]

Reaction temp. (°C)	Amount of "Added-back" water (wt %)	% Cracking	% Isomerization Method I[a]	Calcd. by Method II[a]
200°	0	52.83	6.99	14.8
	0.0126	66.62	5.59	16.7
	0.0251	65.01	6.93	19.8
	0.0300	70.35	5.44	18.4
	0.0375	76.24	5.36	21.2
	0.0491	74.03	5.38	20.6
	0.0752	76.16	5.16	21.6
	0.1004	77.23	5.17	22.6
	0.1974	76.12	5.03	21.1
	0.3596	74.30	5.31	20.6
	0	61.47	4.27	11.0
180°	0	21.83	5.62	7.2
	0.0125	37.28	7.16	11.5
	0.0278	41.09	7.64	13.0
	0.0462	49.66	8.28	16.5
	0.0703	46.24	9.93	18.3
	0.0981	53.41	9.22	21.4
	0.1950	55.15	9.97	20.6
	0.3907	44.08	9.73	17.4
162°	0	7.59	1.97	2.13
	0.0123	23.10	5.98	7.8
	0.0291	37.61	6.10	9.8
	0.0500	39.13	7.23	13.3
	0.0715	42.16	7.80	13.5
	0.0997	44.30	7.86	14.1
	0.2000	44.34	8.02	14.2
	0.4479	18.48	9.29	1.4

[a] See footnotes, Table 1.

so-called "induction period" as the amount of added-back water increases.

2-Methylpentane. Table 3 shows the relative composition of products and Table 4, the effect of "added-back" water on the reactions of 2-methylpentane. The plots of relative compositions of the isomerized products *versus* the amount of added-back water is shown in Fig. 5. The results for isomerization are in good agreement with the data obtained by Hindin, Oblad, and Mills (*3*). However, the percent cracking as a function of added water vapor (Fig. 6) was considerably different from that observed in their investigation. For the 2-methylpentane reaction a sharp optimum for added-back water was observed at about 0.05 wt % for both isomerization activity and cracking activity as shown in Figs. 5 and 6. In contrast to this, the optimum amount of added-

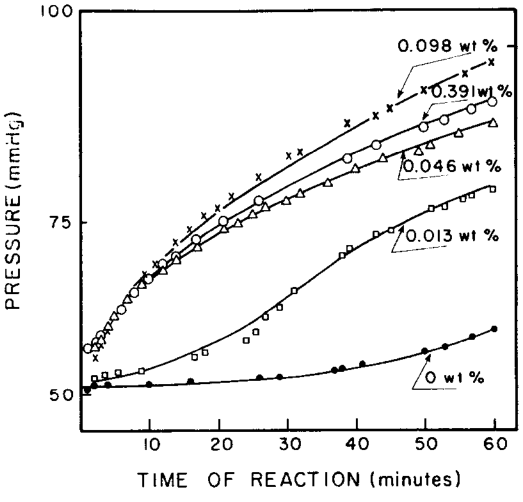

FIG. 4. Pressure versus time in triptane cracking reaction with different amounts of added-back water. Reaction temperature, 180°C.

TABLE 3
COMPOSITION OF THE PRODUCTS FROM THE CRACKING AND ISOMERIZATION OF 2-METHYLPENTANE[a]

Added-back water (wt %)	Hydrocarbon product	Mole fraction	Total % conversion[b]
0	iso-C_4	Negligible	0.0 (C)[b]
	iso-C_5	Negligible	—
	2,3-Me_2C_4	Negligible	—
	3-MeC_5	0.0118	1.185 (I)[b]
	2-MeC_5	0.9885	—
0.04712	iso-C_4	0.006	1.08 (C)
	iso-C_5	0.0048	—
	2,3-Me_2C_4	0.0275	—
	3-MeC_5	0.1856	21.31 (I)
	2-MeC_5	0.7761	—
0.2019	iso-C_4	—	0.42 (C)
	iso-C_5	0.0042	—
	2,3-Me_2C_4	0.0131	9.46 (I)
	3-MeC_5	0.0815	—
	2-MeC_5	0.9013	—

[a] Reaction temp., 100°C; reaction time, 60 min; 6.037 g of catalyst.

[b] As defined in Table 1, footnote *c*.

back water for triptane was about 0.15 wt % though actually little change in cracking and especially in isomerization of the triptane occurred at water contents in excess of about 0.05% "added-back" water.

n-Heptane. The compositions of the products from the cracking of *n*-heptane were calculated by combining two analyses designated as PA_3 and PA_4 and are tabulated in Table 5. It will be noted that the olefins are in much higher concentrations in the cracking products from heptane than in those (Table 1) from triptane. This is reasonable since olefins are probably gradually destroyed by hydride ion transfer during a cracking run. In the circulatory system used for heptane, a 1 hr run corresponds to only a few minutes time of contact. Thus, it would be expected that the triptane products after 1 hr in a static system would, as observed, have much smaller quantities of olefin left than would heptane products with only a few minutes actual time of contact.

The percent isomerization was noticeably smaller than the cracking being in the range 0.21% to 0.8% at 250°C.

The effect of added-back water on the reaction is shown in Table 6 and also in Fig. 7. The amount of optimum added-back

TABLE 4
PERCENT CONVERSION OF 2-METHYLPENTANE UNDER VARIOUS CONDITIONS

Reaction temp. (°C)	Reaction time (min)	Amount of added-back water (wt %)	% Cracking	% Isomerization
100°	60	0.0	0.0	1.185
		0.0263	1.0	12.52
		0.0471	1 08	21.31
		0.0974	0.75	18.18
		0.2019	0.42	9.46
		0.5107	—	1.82
76°	60	0.0510	—	2.4
64.5°	120	0.0498	—	0.147
	180	0.0498	—	0.631

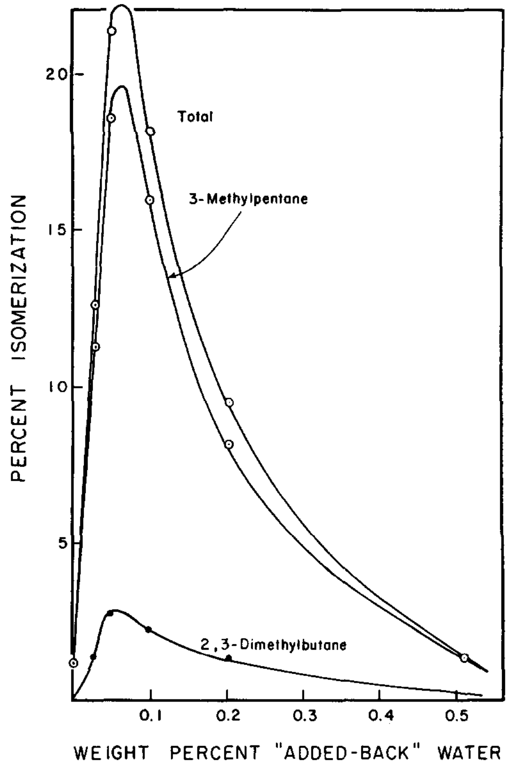

FIG. 5. Percent isomerization of 2-methylpentane as a function of the amount of added-back water. Reaction temperature, 100°C. Reaction time, 60 min.

water for cracking of *n*-heptane is about 0.15 wt %; however, as for triptane, there is little change in the rate of cracking as added-back water increases from about 0.07% up to 0.3%. The maximum increases in the percent cracking of *n*-heptane at 300° and 250°C are about 2.4- and 5.1-fold, respectively. At 200°C, however, there was no appreciable amount of cracking for the first 60 min when the catalyst was dry, as has been shown in Fig. 8. This, apparently, means that the "induction period" is longer than 60 min. This observation that the increase in the activity upon addition of water vapor is greater at lower temperatures is in good agreement with the triptane results.

The relative rates of cracking at 200°C under "dry" conditions compared to cracking on a catalyst to which water has been added-back are very different for *n*-heptane as compared to triptane. Thus per 6.037 g of catalyst, 18.9% heptane would have been cracked in 1 hr at 200°C on a catalyst to which 0.15% water was added back. This is 24% of the value for triptane cracking (72%). On the other hand, for a dry catalyst the cracking of heptane in 60 min is only a few tenths of a percent compared to 5.5% for triptane. In Table 7, it is shown that heptane would be expected to crack about 20% as fast as triptane at 200°C based on the assumption that the 1:2:20 ratio observed by Greensfelder *et al.* (*1*) at 500°C is due to differences in energy of activation for breaking the primary, secondary, or tertiary C–H bonds. It thus appears that adding water vapor results in the normal or expected relative cracking rates for heptane as compared to triptane at 200°C.

TABLE 5
RELATIVE COMPOSITION OF THE PRODUCTS FROM THE CRACKING OF *n*-HEPTANE[a]

	Mole % of product	
Hydrocarbon product	When added-back water is 0.0%	Added-back water is 0.093 wt %
Methane	Trace	Trace
Ethane	0.105	0.031
Ethylene	0.390	0.118
Propane-propylene[b]	4.501[b]	16.465[b]
Iso-butane	3.663	22.236
1-Butene Iso-butene	1.300	0.425
n-Butane	0.550	2.111
2-Butene	0.117	Trace
Iso-Pentane	0.525	3.017
n-Pentane	0.068	0.318
2-Methyl-2-butene	0.700	Trace
2,3-Dimethylbutane	0.026	0.096
2-Methylpentane	0.067	0.386
3-Methylpentane	0.035	0.234
n-Hexane	0.016	0.091
2,4-Dimethylpentane	Trace	0.053
2-Methylhexane	0.068	0.215
2,3-Dimethylpentane	0.062	0.053
3-Methylhexane	0.078	0.242
n-Heptane	88.204	54.288

[a] Reaction temp., 250°C; reaction time, 60 min; 5.22 g catalyst.

[b] With 0.0% water added-back the C_3 fraction was 67.05% propane; with 0.093 wt % added-back water, the C_3 fraction was 94.03% propane.

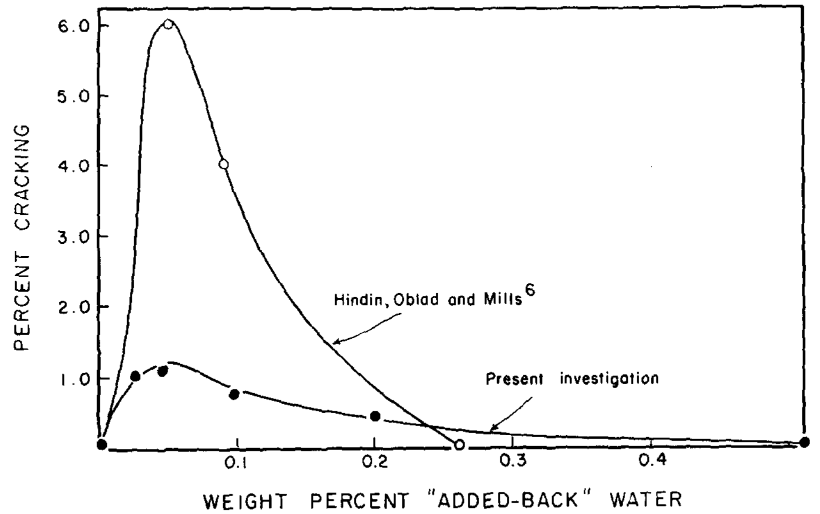

FIG. 6. Percent cracking of 2-methylpentane as a function of the amount of added-back water at 100°C and 60 min.

As is shown in Fig. 7, the percent propylene in the mixture of propane and propylene in the products decreased as the amount of added-back water increased. This is really not surprising since propyl carbonium ions would be expected to be converted into propane as a step in the formation of heptyl carbonium ions that lead to cracking. The real question is how the added water results in more propyl carbonium ions.

The data in Figs. 9 and 10 may throw some light on this point. Clearly, at the start of the cracking reaction in Fig. 9, the

TABLE 6

PERCENT CONVERSION OF *n*-HEPTANE UNDER DIFFERENT CONDITIONS

Reaction temp. (°C)	Reaction time (min)	Amount of added-back water (wt %)	% Cracking	% Isomerization
300°	60	0.000	24.88	0.289
		0.1628	60.39	Trace
250°	60	0.000	6.94	0.210
		0.0107	18.66	0.771
		0.0304	26.41	0.760
		0.0491	30.14	0.711
		0.0697	33.63	0.662
		0.0953	34.54	0.677
		0.1961	35.57	0.499
		0.3213	32.03	0.478
200°	180	0.000	7.94	0.637
	120	0.000	2.58	0.322
	60	0.1510	16.34	1.473
151°	360	0.1514	0.93	0.234[a]

[a] It is interesting to note that although the total isomerization was small in this run at 151°C, all of the C_7 saturated isomers were detected by using a flame-conductivity detector on the chromatographic column. Out of a total of 39 units (0.23 mole %) of isomers, 2-methylhexane and 3-methylhexane amounted to 13.5 and 11.3 units, respectively; 2,3-dimethyl- and 2,3-dimethylpentane, to 6.34 and 4.69 units; and 2,2,3-trimethylpentane, 2,2-dimethylpentane and 3,3-dimethylpentane amounted to 0.49, 0.69, and 0.49 units, respectively.

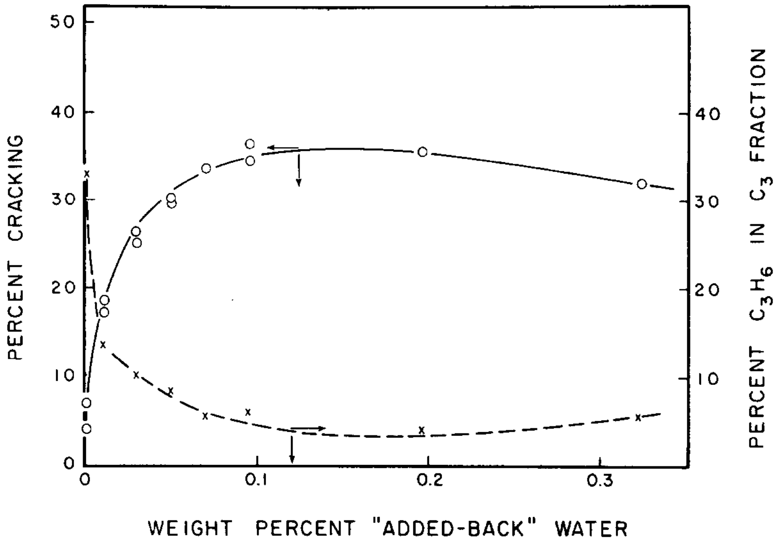

FIG. 7. Percent cracking of *n*-heptane at 250°C for 60 min and the percent propylene in the C_3 fraction as a function of the amount of added-back water.

propylene percentage is near 50% in the propylene-propane mixture. This would be expected if one assumes an equal probability of the charge on the heptyl carbonium ion being on the second as compared to the third carbon atom. In the absence of added water, the decrease in the percentage propylene is gradual as the time of the run increases. With added water vapor the decrease in the percent propylene is rapid. It should be noted incidentally that for the data in Fig. 10, the partial pressure of propylene is approximately constant after about 10 min whereas in the run in Fig. 9 (no added water vapor) the partial pressure of propylene increases throughout the run. This merely indicates that in the presence of added-back water vapor, the consumption of propylene by alkylation, polymerization, and conversion to propane reaches a steady state at which the production of propylene equals its consumption. The real question still remains as to why the added-back water vapor increases the rate of cracking.

Study of n-Heptane Chemisorption by the Radioactive Tracer Method

Six radioactive tracer runs were made on *n*-heptane. The results are all shown in Table 8 Runs 700, 702, and 704 were made on "dry" samples, that is, on samples to which no water was added back after the

TABLE 7

CALCULATED RELATIVE RATES OF CRACKING OF C_7 PARAFFINS AT 200° AND 550°C

Hydrocarbon	No. of hydrogens corresponding to primary, secondary, and tertiary positions P	S	T	Ratio of the rates of cracking relative to triptane 200°C[a]	550°C[b]
n-Heptane	6	10	0	0.1987	0.7429
2-Methylhexane 3-Methylhexane	9	6	1	1.0708	1.1714
2,3-Dimethylpentane 2,4-Dimethylpentane	12	2	2	1.9429	1.6000
2,2-Dimethylpentane 3,3-Dimethylpentane	12	4	0	0.1279	0.5714
2,2,3-Trimethylbutane	15	0	1	1.0000	1.0000

[a] Calculated by using the relative value of P:S:T = 1:3.34:183.3. See text.

[b] Calculated by using the relative value of P:S:T = 1:2:20.

TABLE 8

EFFECT OF WATER ON THE AMOUNT OF CHEMISORPTION OF n-HEPTANE-1-^{14}C[a]

Run no.:	700	701	702	703	704	705
Amount of added-back water (wt %)	0	0.1	0	0.1	0	0.1
Time of chemisorption (min)	180	180	60	60	60	60
Evacuation time for removing physical adsorption (hr)	9	9	9	9	9	9
Evacuation temperature (°C)	110	110	110	110	79	79
Volume of n-heptane used for the exchange reaction (cc STP)	7.962	8.085	8.014	7.962	8.056	8.009
Time of exchange (hr)	7	7, 12, 20	12	11	12	12
Counting rate of exchange of n-heptane (cpm)	40.4	41.2, 46.2, 48.3	32.7	24	207.1	181.7
Volume[b] of exchangeable chemisorption (V_E), (cc STP × 10^3)	7.94	8.85[c]	6.35	4.71	39.89	35.34
Ratio of V_1 to V_2	0.591	1.18	0.272	0.846	2.63	2.89
Counting rate of carbon dioxide (cpm)	295.6	145.6	165.4	72.1	102	102
Volume[b,d] of nonexchangeable chemisorption V_{NE} (cc STP × 10^3)	18.514	9.120	10.363	4.517	6.386	6.386
Total volume[b] of chemisorption ($V_E + V_{NE}$) (cc STP × 10^3)	26.451	17.970	16.713	9.227	46.276	41.726
Molecular flow for the Type 2 chemisorption, k_2 ($\text{min}^{-1} \times 10^3$)	5.483	6.667	4.836	6.103	5.846	5.967
Mass flow for the Type 2 chemisorption R_2 (cc/min × 10^5)	2.736	2.707	2.414	1.557	6.424	5.418

[a] At 110°C and 10 mm Hg on 5.22 g of catalyst.

[b] In cc STP for 5.221 g of catalyst.

[c] Calculated from the data obtained by 12-hr exchange.

[d] Calculated by using the calibration value for n-heptane-1-^{14}C and the correction factor.

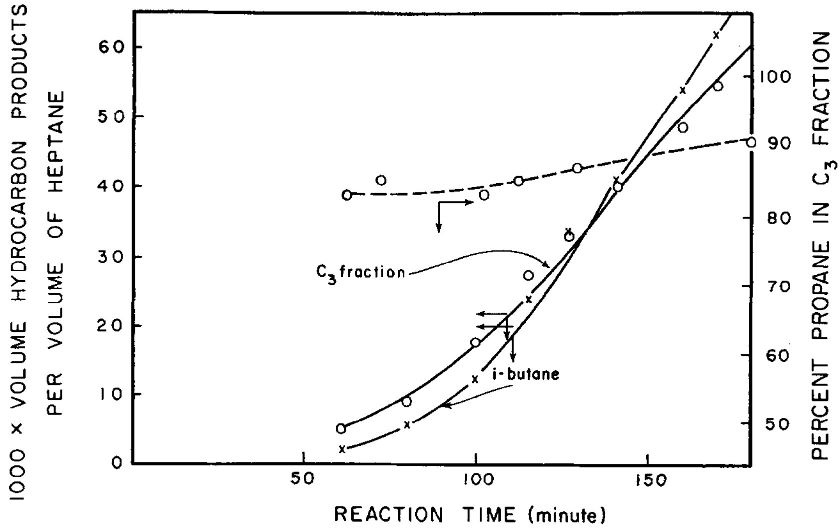

FIG. 8. Gas-phase composition during the catalytic cracking of n-heptane at 200°C. Amount of added-back water: 0 wt %.

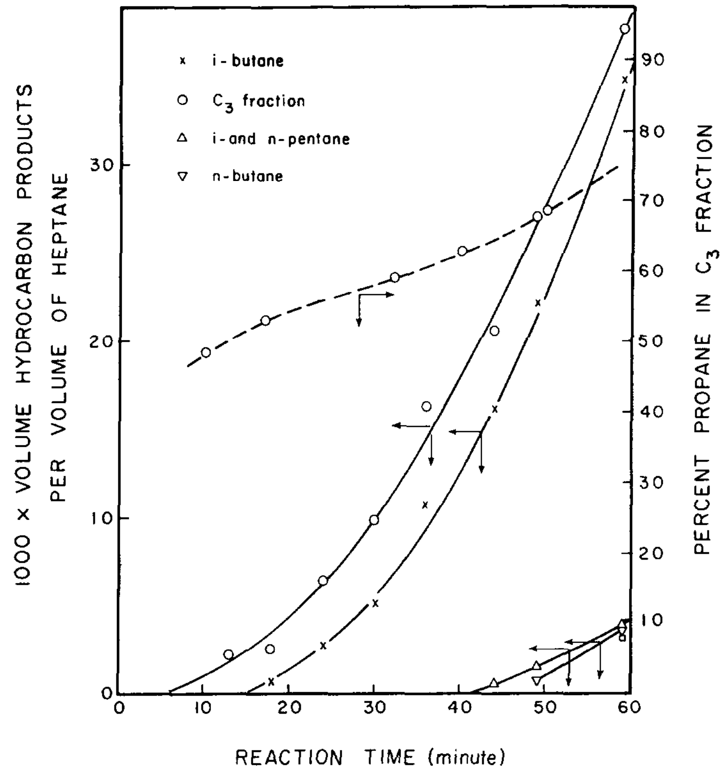

FIG. 9. Gas-phase composition during the catalytic cracking of *n*-heptane at 250°C. Amount of added-back water: 0 wt %.

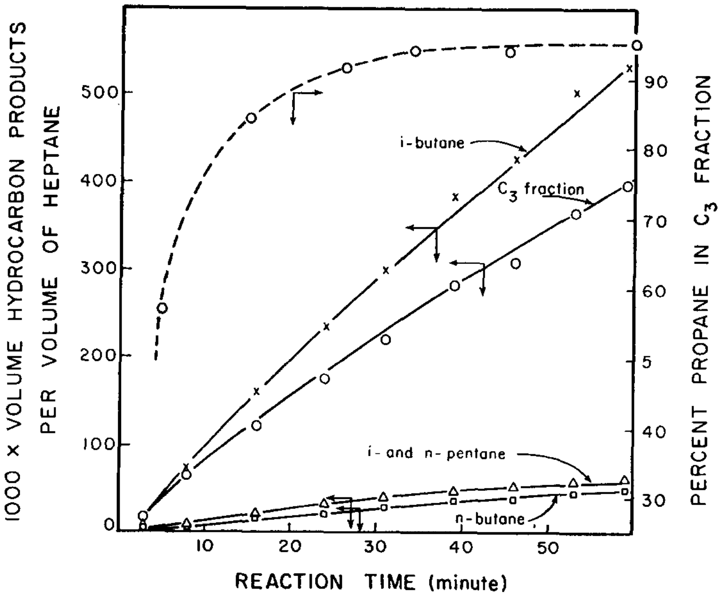

FIG. 10. Gas-phase composition during the catalytic cracking of *n*-heptane at 250°C. Amount of added-back water: 0.1962 wt %.

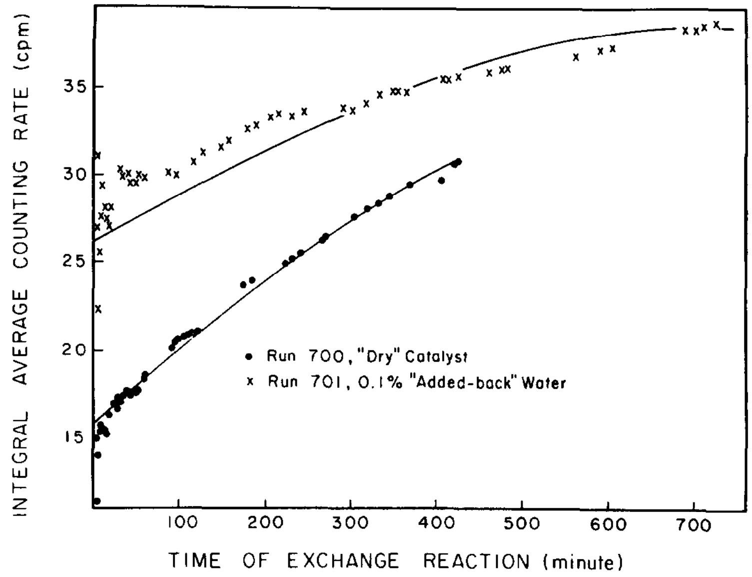

FIG. 11. Integral average counting rate versus time of exchange reaction for heptane.

usual burn-off in oxygen at 535°C and the evacuation at about this temperature. Runs 701, 703, and 705, on the other hand, were made on samples to which 0.1% water was added-back. The results can be illustrated, as in Figs. 11, 12, and 13, by the data for runs 700 and 701. Figure 11 shows an "integral average count" plotted against time. Clearly, there is a considerable amount of practically instantaneous exchange followed by a slow exchange. The instantaneous exchange is, for convenience, called Type 1; its volume is given as V_1. The slower exchange is called Type 2 and its volume labeled V_2. In addition there is a certain amount of nonexchangeable chemisorption that is measured as radioactive carbon dioxide after being burned off in oxygen at 535°C.

Figure 12 is the conventional instan-

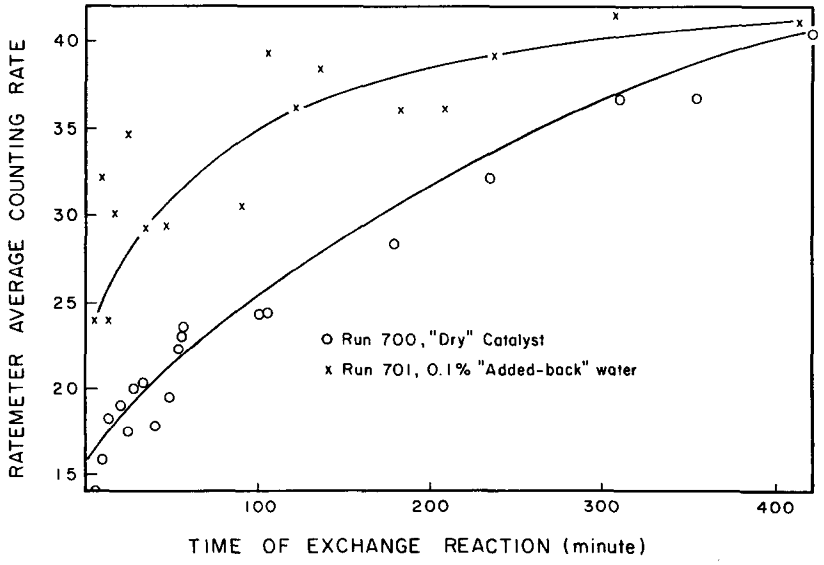

FIG. 12. Rate meter average counting rate versus time of exchange reaction for heptane.

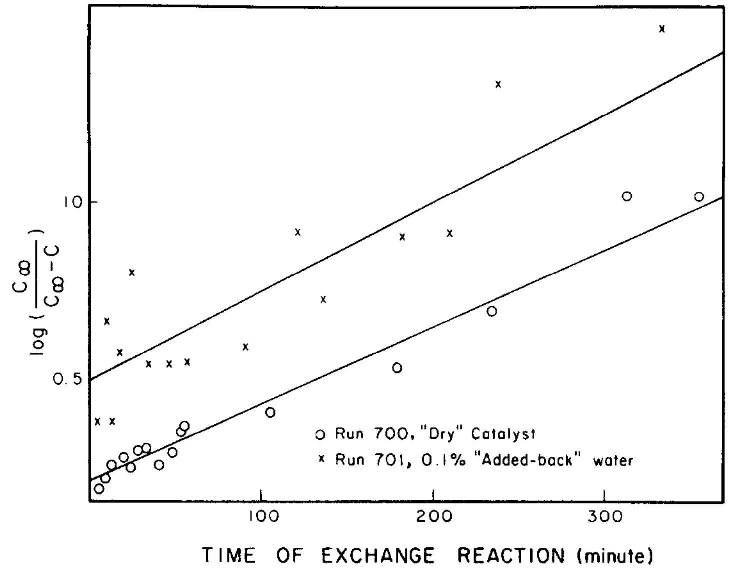

FIG. 13. Plots of log $[C_\infty(C_\infty - C)]$ versus time of exchange reaction for heptane.

taneous counting rate plotted against time. It is the type of curve obtained by taking rate meter readings regularly as a function of time. Finally, in Fig. 13 are plotted the logarithms of $C_\infty/(C_\infty - C)$ against time. This yields the transport rate constant k_2 and the transport rate R_2 as explained above.

The amount of Type 1 adsorption is taken as the zero time extrapolation of the main portion of the exchange curves. As shown in Fig. 14, this Type 1 adsorption seems to increase on the addition of water vapor. However, it is difficult to estimate the amount of Type 1 and impossible to get a value for its rate of exchange. The total amount of Type 1 is rendered uncertain by the fact that some of it may be pumped off during the 9-hr evacuation at 110°C. When a lower temperature of evacuation was used, a considerable amount of purely physical adsorption was almost certainly left on the catalyst in addition to an unknown amount of Type 1. Both the remaining physical adsorption and the true Type 1 adsorption are, of course, reported in the adsorption values in columns 6 and 7 of Table 8.

As is obvious from Table 8 and Fig. 14, the added-back water tends to increase the amount of Type 1 chemisorption, and to decrease or leave unchanged the amounts of Type 2 and nonexchangeable chemisorption. The decrease in the slowly exchanged chemisorption on addition of water is in agreement with the observations of Larson and Hall; however, the increase in Type 1 chemisorption and the decrease in the irreversible chemisorption on addition of water are contrary to their observations and those of MacIver and Emmett (*14*). In any event, the total chemisorption is quite small, being about 0.0016 cc/g for the sum of Types 1 and 2 and up to 0.003 cc of irreversible adsorption per gram. Clearly, the only connection between the measured chemisorption and the cracking activity is the slight increase in Type 1 adsorption with added-back water. Considering the uncertainty in the fraction of the total Type 1 adsorption that is being measured and the uncertainty of the rate of Type 1 adsorption, one cannot say with certainty whether or not the water acts to increase the cracking rate by virtue of increasing the amount or rate of Type 1 chemisorption.

Finally, a few remarks in regard to the purity of the radioactive heptane are in order. Before run 700 and two months after run 705, radiochemical impurity tests were made on the supply of radioactive heptane. The results shown in Table 9 clearly indicate some radioactive decomposition of the heptane during storage. Initially no heptenes

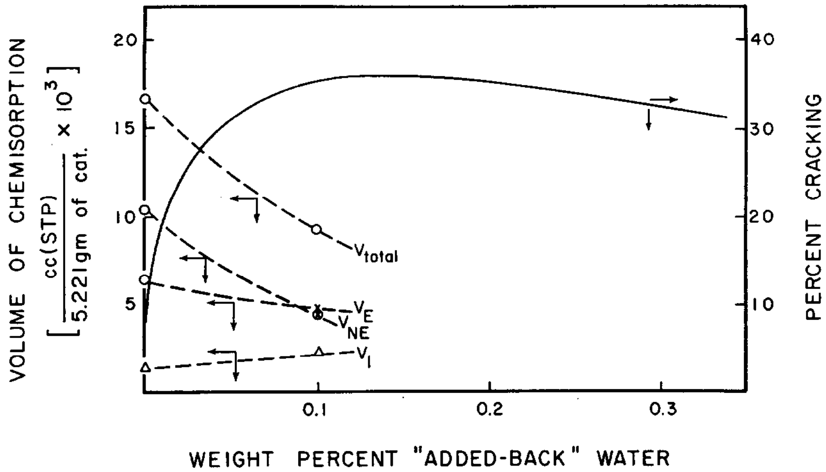

FIG. 14. Effect of added-back water on the percent cracking of *n*-heptane at 250°C and the volume of 60-min chemisorption at 110°C and 10 mm Hg. V_I refers to Type 1 chemisorption; V_E, the sum of Type 1 2 chemisorption; V_{NE}, the nonexchangeable adsorption; and V_{total}, the sum of Type 1, Type 2, and V_{NE} chemisorptions.

were detectable on the purified material by flame-conductivity gas chromatography. Probably the small amount (0.12%) of radioactivity that came out of the chromatograph at the point corresponding to heptene was actually the tail end of the heptane curve. It seems that the impurity content was not serious in the original material. On the other hand, after approximately 2 months some radiochemical decomposition had occurred. As a result only 95.4% of the radioactivity was actually in heptane after the 2 months. All six radiotracer runs were completed in the first 3 weeks so it is unlikely that decomposition products from the heptane seriously interferred. In any event, even if part of the chemisorption were due to traces of heptene, the results clearly show that the chemisorption is very small and that water vapor does not increase any portion except possibly the Type 1 adsorption.

One other set of tests is of interest in connection with the question of the extent of decomposition during the adsorption runs. In Table 10 are shown the analyses of the radioactive heptane pumped off at the end of the adsorption step (A runs) in two runs and the analyses of the desorbed radioactive heptane (B runs) in three runs. Clearly, some decomposition occurred on the dry catalyst during the 3-hr chemisorption and during the 9-hr evacuation and 12-hr exchange. The only serious contaminant might be the heptenes and the amount of these is almost certainly considerably smaller than shown in Table 10 because of the tendency of the heptane curve to tail out over the region at which the heptenes would be expected on the chromatograph. Also the

TABLE 9

RADIOCHEMICAL IMPURITY TESTS OF *n*-HEPTANE-1-^{14}C BEFORE RUN 700 AND AFTER RUN 705

Before run 700		After run 705	
Hydrocarbons	% Radioactivity	Hydrocarbons	% Radioactivity
Methane to iso-butane range	0.12	Methane to *n*-pentane range	2.721
n-Butane to *n*-hexane range	0.65	*n*-Pentane to *n*-hexane range	0.325
Iso-heptane and *n*-heptane	99.11	*n*-Hexane to *n*-heptane range	0.376
Heptenes	0.12	*n*-Heptane	95.433
		Between *n*-heptane and 1-heptene	0.515
		Heptenes	0.630

TABLE 10

RADIOCHEMICAL ANALYSES OF n-HEPTANE-1-^{14}C AFTER USE FOR THE CHEMISORPTION STEP (A) AND FOR THE EXCHANGE STEP (B)

	% Radioactivity		
Hydrocarbons	Run 700A	Run 701A	
Methane to n-hexane	7.363	0.383	
Isoheptanes	0.267	0.112	
n-Heptane	91.5	99.25	
Heptenes	0.872	0.253	
	Run 700B	Run 701B	Run 704B
Methane to n-hexane	0.062	0	2.05
Isoheptanes	0.308	0	1.84
n-Heptane	98.662	100	95.29
Heptenes	0.968	0	0.82

observed heptene values could represent a portion of the chemisorbed heptane (as heptyl carbonium ions) tending to desorb as heptene even at 110°C. In this connection, it is very striking that the impurity level in the heptane recovered during the runs in which the catalyst contained added-back water are much smaller than for the "dry catalyst." Presumably, the decomposition indicated in Table 10 is mostly radioactive decomposition of the adsorbed molecules; this is apparently slowed down by the added-back water.

DISCUSSION

On the basis of the present work on heptane and the previous work on isobutane adsorption as measured by radioactive tracer methods, it seems clear that the marked accelerating effect of added-back water vapor on the cracking and isomerization of hydrocarbons over a silica-alumina catalyst cannot be explained with certainty as being due to either the increase in the amount or the rate of chemisorption of the hydrocarbon. A possible exception to this is the Type 1 adsorption observed for heptane at 110°C, but the rate of exchange is so fast as to render quantitative measurements impossible. Certainly the major reversible chemisorption (Type 2) is either inhibited by added-back water or left unchanged.

One other possible explanation of the influence of added-back water on the cracking rate seems plausible. Peri (*27*) and also Leftin and Hall (*28*) have supported the idea that "added-back" water instead of being localized on Lewis sites may move freely over the catalyst surface. If this is true it seems reasonable that a polarized water molecule approaching or coming in contact with a carbonium ion of the reactant may have an accelerating influence on the rate of scission of the chemisorbed hydrocarbon. For example, in the scission to produce propylene and a butyl carbonium ion from heptyl carbonium ion the actual breaking away of the propylene may be helped by the presence of a polarized water molecule adjacent to the heptyl carbonium ion. It is, of course, recognized that heptyl carbonium ions might be driven off again as unreacted heptane unless the chance of scission is practically unity for each chemisorption. If added-back water vapor by being adjacent to the chemisorbed hydrocarbon makes the scission process more likely, it can in effect increase the rate of cracking without increasing either the rate of chemisorption or amount of chemisorption of the parent hydrocarbon. More work would be needed to make clear whether or not this latter explanation is really operative.

ACKNOWLEDGMENT

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