[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Racemization, Isomerization and Isotopic Exchange of (+)3-Methylhexane on a Silica–Alumina Catalyst[1]

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This paper deals mainly with isotopic exchange with heavy water, with racemization and with isomerization of (+)3-methylhexane on silica–alumina catalysts at −4 to 240°. At 200 and 240°, molecules issue from the reaction devoid of rotation and in isomeric equilibrium with respect to 2- and 3-methylhexane, 2,3- and 2,4-dimethylpentane and 3-ethylpentane. All molecules which have reacted are extensively exchanged and all hydrogen atoms save one tertiary are available for exchange. As temperatures are lowered, dimethylpentanes no longer appear and the quantities of 2-methylhexane fall progressively below that corresponding to equilibrium with product (±)3-methylhexane. At −4 and 56°, racemization greatly exceeds isomerization and also isotopic exchange. At 120°, migration of ethyl or propyl groups seems as important as that of methyl. At low temperatures two different types of sites are involved and crevice sites seem indicated. Identity of rates in the presence and absence of hydrogen indicate that chain initiation does not involve equilibrium formation of hydrogen.

Evidence for the carbonium ion theory of reactions of hydrocarbons on cracking catalysts[2,3] is primarily analogical. Cracking catalysts are strong acids. A number of reactions which occur on cracking catalysts closely resemble those promoted by strong acids such as aluminum chloride or sulfuric acid: alkylation, skeletal isomerization, polymerization, isotopic exchange, etc. In its totality, this evidence for carbonium ion processes is strong, but many features require further elucidation.

A study of the behavior of an optically active hydrocarbon on a silica–alumina catalyst offers some prospect of contributing to such elucidation. The reactions of optically active 3-methylhexane in the presence of sulfuric acid,[4] halosulfonic acids[5] and aluminum bromide[6] have been studied. These reactions, which are clearly carbonium ion in nature present a model with which the reactions on solid acidic catalysts could be compared. The research reported in the present paper followed that with sulfuric and halosulfonic acids as closely as possible. It involves primarily a study of the simultaneous isomerization, isotopic exchange and racemization reactions on a silica–alumina catalyst at temperatures of −4 to 240°.

Experimental

Materials.—The silica–alumina catalyst, Houdry Type S-45 cracking catalyst, 12.5% alumina, 87.5% silica, was supplied by Dr. A. G. Oblad. It was crushed and sieved to 20–40 mesh.

The preparation of inactive methylhexanes[4a] and of (+)3-methylhexane[7] has been described. Phillips Petroleum Company Pure Grades of 2,4-dimethylpentane, 2,3-dimethylbutane and heptane and the Research Grade of methylcyclopentane were employed. All alkanes were percolated through silica gel which had been heated in nitrogen to 350° before use. All alkanes agreed well with standard samples of the National Bureau of Standards in differential infrared spectroscopy. 2-Methyl-1-hexene was prepared by coupling the Grignard reagent of propyl bromide with 2-methyl-3-chloropropene, b.p. 90–91°, n^{20}_D 1.4034. All hydrocarbons which had been prepared by the Grignard reaction were stored over sodium to remove traces of halogen before final purification.

Apparatus.—**Apparatus A** was of the Schwab type.[8] A U-tube of 3 mm. capillary was surmounted on the evaporation side by a 25-cc. mixing bulb and then the catalyst chamber. The exit tube from the catalyst chamber, in the form of an inverted U, led to the top of a water cooled condenser which was connected to the top of the return side of the capillary U-tube. Just below the condenser a side tube led to a gas buret and a vacuum manifold *via* a spherical joint. The capillary U-tube was then filled with alternating slugs of water and hydrocarbon. In most cases 2.6 cc. of hydrocarbon and either 0.1 or 0.5 cc. of water was used.

In operation, the furnace was heated to the operating temperature while raised above the catalyst chamber. It was then lowered to cover the catalyst chamber, the mixing bulb and the top of the capillary. The hydrocarbon and water boiled, passed through the catalyst bed, condensed in the condenser (the exit tube from the catalyst chamber was warmed electrically) and flowed into the capillary U-tube where alternate slugs of hydrocarbon and water reformed. The recycling time was about 20 minutes.

At the conclusion of a run, hydrocarbon and water were removed by vacuum distillation to a trap connected at the spherical joint.

Save as otherwise indicated, 10 cc. of catalyst was used and a fresh sample in each run. Fresh catalyst was evacuated 4 hr. at 450°, cooled and dry nitrogen admitted. Before a new run, previously used catalyst was evacuated one hour at room temperature.

Apparatus B was similar but the capillary U-tube was shorter, 2.1 cc. of hydrocarbon was employed and 0.1 or 0.4 cc. of water.

The use of heavy rather than of light water led to isotopic exchange with the hydrocarbon. However, particularly with 0.1 cc. of heavy water, the ratio of total deuterium to total hydrogen was small and isotopic dilution made interpretation of isotopic exchange patterns somewhat difficult.

Apparatus C was designed to minimize isotopic dilution. A stream of nitrogen or hydrogen was passed through a saturator containing heavy or light water and thence through a saturator containing hydrocarbon. The composition of the nitrogen–D_2O–hydrocarbon stream was determined by the temperatures of the two saturators. The vapor stream then passed through the catalyst chamber to a condenser. A separator returned the hydrocarbon phase to the hydrocarbon saturator; the condensed water was withdrawn. Thus, fresh heavy water was continually introduced and, provided that the conversion per pass was small, isotopic dilution was small. It was possible to operate Apparatus C without admission of any air. Small amounts of air inevitably entered Apparatus A and B during the hydrocarbon–water addition. The nitrogen or hydrogen stream in C was passed through hot copper wool and dried before entering the apparatus. Nitrogen saturated with water or heavy water was passed through the apparatus for

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(2) C. L. Thomas, *Ind. Eng. Chem.*, **41**, 2564 (1949).

(3) B. S. Greensfelder, H. H. Voge and G. M. Good, *ibid.*, **41**, 2573 (1949).

(4) (a) R. L. Burwell, Jr., R. B. Scott, L. G. Maury and A. S. Hussey, THIS JOURNAL, **76**, 5822 (1954); (b) G. S. Gordon, III, and R. L. Burwell, Jr., *ibid.*, **71**, 2355 (1949); (c) R. L. Burwell, Jr., and G. S. Gordon, III, *ibid.*, **70**, 3128 (1948).

(5) R. L. Burwell, Jr., L. G. Maury and R. B. Scott, *ibid.*, **76**, 5828 (1951).

(6) H. E. Heller, *ibid.*, **74**, 4858 (1952).

(7) H. C. Rowlinson, R. L. Burwell, Jr., and R. H. Tuxworth, *J. Phys. Chem.*, **59**, 225 (1955).

(8) G. M. Schwab and N. Theophilides, *ibid.*, **50**, 427 (1946).

one hour at reaction temperatures before each run with a new catalyst.

Apparatus D.—At temperatures below 120°, slowness of reaction made the use of any of the procedures described above impractical. At −4 and 56°, experiments were run in sealed tubes. A tube partly filled with catalyst was evacuated at 450°, cooled and filled with the desired amount of hydrocarbon and water by vacuum line techniques. The tube was sealed and rotated at 30 r.p.m. in an oven at 56°. The hydrocarbon was present partly as vapor and partly as liquid in the catalyst pores. The reaction was so slow under these conditions that we feel that diffusion was fast compared to reaction. The hydrocarbon was recovered after reaction by resealing the reaction tube to the manifold and evaporating the hydrocarbon into a cold trap under vacuum.

Analysis.—Polarimetry: we estimate that the probable error of $\Delta\alpha/\alpha_0$ is 0.004. Isomerization of undeuterated samples was determined on the Baird double-beam infrared spectrometer by a method of successive approximations. Initially, the composition of the sample was roughly estimated from its infrared spectrum and a synthetic sample of this composition was made. This synthetic sample was placed in both the reference and the sample cell of the spectrometer and the differential spectrum recorded. The experimental sample was then placed in the sample cell and the spectrum rerun. Using the deviations of this recording from that of the first and using the spectra of the pure components, the composition of the experimental sample was re-estimated and a synthetic mixture of that composition prepared. The sequence was then repeated until the synthetic and experimental samples were substantially identical. Three or four synthetic samples usually sufficed. In the four component system, 2-methylhexane, 3-methylhexane, 2,3-dimethylpentane and 2,4-dimethylpentane, the accuracy was somewhat better than 1% in each component.

In experiments with (+)3-methylhexane, we have assumed that product 2,3-dimethylpentane is optically inactive. Thus, the difference between the loss of rotation and the sum of the percentages of 2-methylhexane, 2,3- and 2,4-dimethylpentanes gives the % of (±)3-methylhexane formed. Samples isomerized in the presence of heavy water could not be analyzed directly since the introduction of deuterium complicates the infrared spectrum (and also the mass spectrum) too much. To check our general conclusions a few samples were analyzed as follows. Following polarimetry, deuterium was removed from the sample by exchange with hydrogen gas over a nickel–kieselguhr catalyst. This does not lead to skeletal isomerization.[7] The sample was then analyzed as described above.

Further details of the apparatus and experimental procedure are presented in the doctoral thesis of H. A. Porte, Northwestern University, 1956, obtainable from University Microfilms, Ann Arbor, Michigan.

Experimental Results

Measurement of loss of rotation of (+)3-methylhexane permits ready measurement of the catalytic activity of silica–alumina catalysts. As will appear, the loss in rotation results from the formation of (±)3-methylhexane, 2-methylhexane, 2,3- and 2,4-dimethylpentane. Results with the Schwab type of recirculation apparatus (Apparatus A) are given in Table I.

Effect of Replacing Nitrogen by Hydrogen.—Experiments were run with Apparatus C to discover the effect of replacing nitrogen as the carrier gas by hydrogen. Fresh samples of catalyst (20 cc.) were evacuated at 500° for 8 hr. in each run. The carrier gas rate was about 900 cc. per hour, and both saturator temperatures were 75°. The saturator contained 2.6 cc. of hydrocarbon. The approximate vapor composition was 60% hydrocarbon, 25% nitrogen and 15% water. The following losses in rotation were observed in successive four hour runs at 200°: nitrogen, 0.123; hydrogen, 0.105; hydrogen, 0.119; nitrogen, 0.165; nitrogen, 0.106; hydrogen, 0.079. Although the reproducibility is poor, it is clear that nitrogen and hydrogen give rates of the same general order of magnitude. The last run was repeated with hydrogen and without change of catalyst, 0.052, and then with nitrogen, 0.029.

Isomerization.—Results of the isomerization of (+)3-methylhexane and 2,3-dimethylpentane are shown in Table II. No components other than 2- and 3-methylhexane and 2,3- and 2,4-dimethylpentane could be detected by infrared spectroscopy. At 325°, mass spectroscopy indicated about 1% of aromatics and some disproportionation to higher and lower molecular weight hydrocarbons.

TABLE I

LOSS OF ROTATION OF 3-METHYLHEXANE

Run no.	Water, cc.	Temp., °C.	Time, hr.	$\Delta\alpha/\alpha_0$	$\frac{1}{t}\ln(\alpha_0/\alpha)$[a]
1A	0.1 H_2O	200	0.5	0.166	0.361
2A			1.0	.282	.333
3A			4.0	.554	.202
4A			4.0	.522	.183
5A			24.0	.822	.075
6A	0.1 D_2O	200	4.0	.550	.197
7A	.5 H_2O	200	4.0	.151[b]	.041
8A	.1 H_2O	160	2.0	.254	.147
9A	.1 D_2O	160	2.0	.229	.131
10A	.5 D_2O	160	5.3	.074	
11A	.5 D_2O	160	24.0	.082	
12A	.1 H_2O	240	0.5	.214	.484
13A	.1 H_2O	240	0.75	.274	.428
14A	.1 H_2O	200	1.0[c]	.231	.262
15A			1.0[d]	.226	.255
16A			1.0[e]	.172	.189

[a] First-order rate constant in hr.$^{-1}$ Hydrocarbon volume, 2.6 cc. [b] Highest loss of rotation observed with 0.5 cc. of H_2O at this temperature no matter what the reaction time. Similar experiments at 160°, 4 to 44 hr. gave losses of rotation of 0.07 to 0.1. [c] 0.4 mole % of 2-methyl-1-hexene. [d] 0.9 mole % 2-methyl-1-hexene. [e] 3.7 mole % 2-methyl-1-hexene.

TABLE II

ISOMERIZATION OF (+)3-METHYLHEXANE

Run no.[a]	Temp., °C.	Time, hr.	$\Delta\alpha/\alpha_0$	(±)3MH[b]	2MH[b]	23MP[b]	24MP[b]
17B	240	16	0.70	0.28 (.25)[c]	0.29	0.07	0.06
18B	200	18	.71	.30 (.24)[c]	.29	.06	.06
19A[d]	200	66	.57	.23 (.20)[c]	.24	.05	.05
20B	160	24	.72	.37 (.23)[c]	.28	.04	.03
21A	125	162	.73	.43 (.20)[c]	.27	.02	.01
22D	56	336	.708	.662 (.031)[c]	.046	.00	.00
23B[e]	160	24	...	.113	.114	.572	.201

[a] The upper case letter following the run number indicates type of apparatus employed (see Apparatus). Ten cc. of catalyst and 0.1 cc. of water were used in A and B runs, 20 cc. of catalyst and 0.01 cc. water, in 22D. 2.6 cc. of hydrocarbon were used in A and D runs, 2.1 in B. The catalysts in runs 18B, 21A and 19A had been used, the latter in runs with D_2O. [b] 3MH is 3-methylhexane; 2MH, 2-methylhexane; 23MP and 24MP, 2,3- and 2,4-dimethylpentane. [c] Amount of 3MH in equilibrium with listed amount of 2MH computed from the relation $\Delta F^0 = 436 - 0.55T$ (T in °K., ΔF^0 in cal.), L. G. Maury, R. L. Burwell, Jr., and R. H. Tuxworth, THIS JOURNAL, **76**, 5831 (1954). [d] D_2O, 46.2% of molecules exchanged, total deuterium content, 10.2%. [e] 2,3-Dimethylpentane used as feed.

Isotopic Exchange.—A number of experiments involved heavy water and (+)3-methylhexane. Table III presents a comparison of the loss of rotation with the fraction of the molecules of hydrocarbon which underwent isotopic exchange. The latter quantity was determined mass spectroscopically from the parent peak.[7] An averaged parent peak sensitivity was employed which was appropriate to the particular hydrocarbon composition as estimated from Table II. It was assumed that all 2-methylhexane, 2,3- and 2,4-dimethylpentane were isotopically exchanged. The procedure also assumes that the isotopic distribution patterns are the same for the four hydrocarbons. This was not always true. The resulting error should not affect the sum of the various isotopically exchanged species, the total fraction exchanged. Error in this latter quantity is about ±10%.

In experiments at −4 and 56° in sealed tubes it was impossible to avoid extreme isotopic dilution using our usual procedure. To get adequate rates, added heavy water had to be much less than in experiments at higher temperatures. In the last four experiments of Table III (runs 33D-36D), two tubes each containing 20 cc. of catalyst and on the same manifold were evacuated at 400°. After admission of nitrogen, 0.5 cc. of heavy water was added to the tubes and allowed to stand for two weeks. After evacuation at 400°, this process was repeated. After evacuating at 450°, 0.01 g. of D_2O was added to each tube and, after a week, 1.5 cc. of (+)3-methylhexane and 1.5 cc. of isopentane. In runs 33D and 35D, the isopentane contained 72% deuterium. It had been made by hydrogenating isoprene with deuterium on a nickel–kieselguhr catalyst following which the isopentane was subjected to exchange with deuterium over the same catalyst. Following the reaction period, the samples were subjected to microdistillation following which the methylhexane fraction was analyzed. The observed loss of rotation was corrected for the several % of isopentane which remained as estimated by gas chromatography.

Isotopic exchange patterns are shown in Table IV and Fig. 1. With Apparatus C, the exchange patterns are nearly independent of degree of conversion (compare runs 26C and 27C in Fig. 1), and they exhibit the least effect of isotopic dilution as judged by relative concentrations of highly exchanged species. At low enough conversions, Apparatus A or B gives patterns substantially identical with those of Apparatus C. For example, the pattern of a run with methylcyclopentane on Apparatus A, 0.1 cc. of D_2O, total conversion of 1.5%, was of very nearly the same shape as that of run 39C, Table IV. The effect of isotopic dilution at higher conversions may be seen by comparing in Fig. 1 run 28A (0.1 cc. D_2O) with run 29A (twice with 0.5 cc. D_2O).

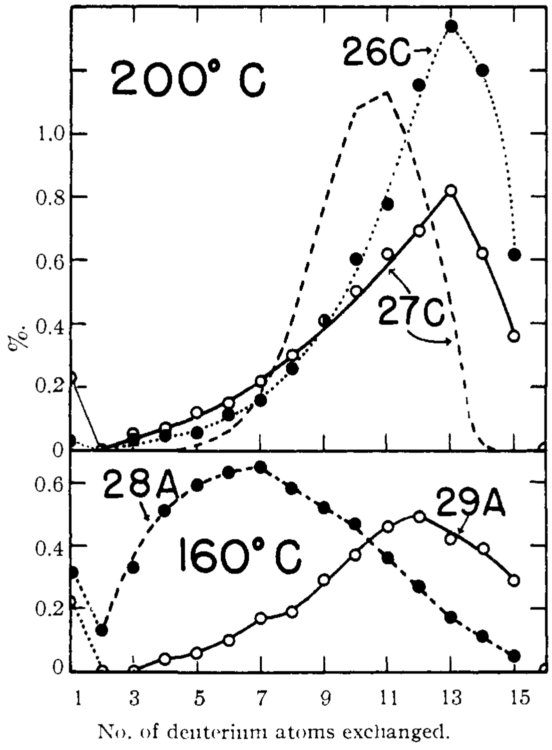

Fig. 1.—Isotopic exchange patterns of 3-methylhexane. In run 26C, $^1/_2$ of the % of each exchanged species is plotted. In run 27C, the dashed line represents the computed random distribution assuming 15 exchangeable hydrogen atoms for a product of the total deuterium content of the actual run 27C, the full line. In run 28A, 0.1 cc. of D_2O was employed. Run 29A is the product of two successive runs on the same material using fresh 0.5 cc. of D_2O in each run. Total % exchanged: 26C, 13.8%; 27C, 5.19; 28A, 5.69; 29A, 3.50.

Table III

Loss in Rotation *vs.* Exchange of (+)3-Methylhexane

Run no.[f]	Temp., °C.	Time, hr.	$\Delta\alpha/\alpha_0$	Fraction exchanged
24A[a]	240	1	0.083	0.071
25A[a]	200	4	.077	.077
19A[b]	200	66	.572	.462[m]
26C[c]	200	4	.140	.138
27C[d]	200	4	.052	.052
28A[b]	160	4	.063	.057
29A[a,i]	160	48	.041	.035
30C[d]	140	7.7	.020	.014
31A[b]	125	21	.032	.030
32C[e]	120	13.5	.020	.015
33D[g,k]	56	24	.33	.25 (0.16)[n]
34D[h,k]	56	24	.27	.12[p]
35D[g,k]	−4	912	.21	.075 (0.038)[n]
36D[h,k]	−4	648	.10	.015

[a] 0.5 cc. D_2O. [b] 0.1 cc. D_2O. [c] Catalyst evacuated 4 hr., 450°. Both saturators at 75°. [d] Both saturators at 75°. [e] Hydrocarbon saturator at 75°, D_2O saturator at 27°. [f] All catalysts had been previously used in runs involving D_2O and were evacuated at room temperature before the listed run save as otherwise listed. Operative details of runs 33D to 36D were different; see text. [g] With deuterated isopentane. [h] With isopentane. [i] Product of 24 hr. run repeated. [k] Product analyzed by gas chromatography. Fraction isomerized to 2-methylhexane: 33D and 34D, 0.02; 35D, 0.01; 36D, 0.005. [m] Should be increased to about 0.53 to allow for extensive isotopic dilution by which some actual exchange was lost. [n] The parenthetical value does not count anomalous d_1. [p] Extensive isotopic dilution causes loss of exchange as in run 19A.

Discussion

The data of the present paper add strong support to the theory that carbonium ion reactions are involved in the reactions of hydrocarbons on silica–alumina catalysts; they set certain limitations upon the nature of the chain initiating step and upon the role of water as a co-catalyst; and the stereochemical data, particularly, afford some information about the nature of the carbonium ion intermediate.

It has been previously established[9-13] that at temperatures of about 150°, isotopic exchange occurs between alkanes containing a tertiary hydrogen atom and deuterated silica–alumina catalysts. Alkanes containing only secondary and primary hydrogen atoms react orders of magnitude more slowly.

In the presence of small amounts of light water, alkanes with a tertiary hydrogen atom isomerize to other alkanes containing tertiary hydrogen atoms[14] and at rates approximately equal to those of isotopic exchange in the presence of heavy water. However, the possibility of an isotope effect prevents exact comparison of rates of isotopic ex-

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(9) R. C. Hansford, *Ind. Eng. Chem.*, **39**, 849 (1947).

(10) R. C. Hansford, R. G. Waldo, L. C. Drake and R. E. Honig, *ibid.*, **44**, 1108 (1952).

(11) S. G. Hindin, G. A. Mills and A. G. Oblad, This Journal, **73**, 278 (1951).

(12) S. G. Hindin, G. A. Mills and A. G. Oblad, *ibid.*, **77**, 538 (1955).

(13) R. G. Haldeman and P. H. Emmett, *ibid.*, **78**, 2922 (1956).

(14) S. G. Hindin, A. G. Oblad and G. A. Mills, *ibid.*, **77**, 535 (1955).

Table IV

Isotopic Exchange Patterns

Run no.	36D	33D[h]	32C[a]	30C[c]	39C[d]	37A[b]	38A[b]
Hydrocarbon[e]	3MH	3MH	3MH	3MH	McP	2MH	24MP
Temp., °C.	−4	56	120	140	200	200	200
D_1, %[f]	0.11	9.2	0.00	0.02	0.31	0.13	0.0
D_2	.20	2.5	.00	.03	.18	.10	.00
D_3	.21	3.2	.01	.01	.28	.20	.04
D_4	.23	2.8	.02	.02	.13	.22	.10
D_5	.22	3.0	.05	.02	.25	.26	.12
D_6	.19	2.1	.07	.04	.42	.25	.12
D_7	.15	1.5	.11	.11	.74	.27	.16
D_8	.11	0.4	.12	.08	1.01	.31	.16
D_9	.06	0.0	.15	.11	1.43	.25	.25
D_{10}	.03		.18	.14	1.68	.25	.28
D_{11}	.00		.20	.15	1.21	.25	.36
D_{12}			.22	.23	0.08	.22	.33
D_{13}			.22	.13		.21	.23
D_{14}			.11	.09		.21	.14
D_{15}			.07	.16		.20	.08
D_{16}			.01	.01		.00	.00
% Exchanged	1.5	24.7	1.5	1.4	7.7	3.3	2.4

[a] Hydrocarbon saturator at 75°, heavy water saturator at 27°. [b] 0.5 cc. D_2O, 2.6 cc. hydrocarbon. [c] Both saturators at 75°. [d] Both saturators at 55°. [e] 3MH is 3-methylhexane; 2MH, 2-methylhexane; 24MP, 2,4-dimethylpentane; McP, methylcyclopentane. [f] The error in D_1 is relatively large because of correction for species containing ^{13}C. [g] With deuterated isopentane, see text.

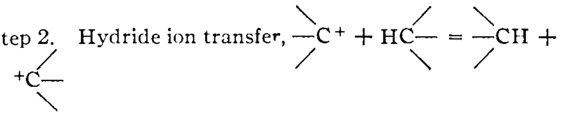
change and isomerization. Further, that unknown fraction of reactant which is re-formed at the end of the reaction sequence contributes to exchange but not to isomerization. The use of optically active 3-methylhexane has enabled us to obviate both difficulties.

We have worked primarily under flow, recycle conditions (runs indicated A, B or C) but at 56 and −4° we employed sealed-tube reactions (indicated by D). It is difficult to obtain exact reproducibility with this catalyst,[13] but our conclusions depend either upon gross differences in rate or upon relative differences in rates of simultaneous reactions. These relative rates were insensitive to variations in gross rate.

Our results present marked analogies to those with sulfuric acid,[4,5] and a general similarity of mechanism is evident.

Step 1. Formation of a carbonium ion

Step 2. Hydride ion transfer,



Step 3. Chain termination

Step 2′. Isotopic exchange of the carbonium ion

Step 2″. Isomerization of the carbonium ion

Results at 200–240°.—We present first the essential results at the higher temperatures followed by comments on them.

(1) At 200 and 240°, the (+)3-methylhexane which reacts appears as a substantially equilibrium mixture of (±)3-methylhexane, 2-methylhexane, 2,3- and 2,4-dimethylpentane and, probably, 3-ethylpentane.

(2) Any heptanes without tertiary hydrogen atoms such as heptane or *gem*-dimethylpentanes are formed at rates less than 0.01 of the other isomers. However, isomerization to and reaction of analogous compounds can be detected in the system, cyclohexane = methylcyclopentane. The rate of Step 2″ of the latter compound is about $^1/_{500}$th that of Step 2 or of Step 2′.

(3) The products of reaction of tertiary hydrocarbons in the presence of heavy water are deeply exchanged isotopically but perdeuterohydrocarbons are formed to a negligible extent. Thus, all hydrogen atoms are available for exchange except, presumably, the hydrogen atom added to the carbonium ion by hydride ion transfer, Step 2. These isotopic exchange patterns are shown in Table IV and Fig. 1. As exemplified in Fig. 1, the exchange patterns are broader than the statistical. Exchange patterns at 160° differ but little from those at 200°.

(4) Every molecule which reacts in the presence of heavy water is both isotopically exchanged and converted to an optically inactive or racemic product.

Comments. (1).—Results of isomerization of (+)3-methylhexane are presented in Table II. The degree of loss in rotation exceeds that of isomerization and this excess is entered as fractional formation of (±)3-methylhexane.[15] At 200 and 240° (runs 17, 18, 19) (±)3- and 2-methylhexane appear in substantially their equilibrium ratio. The equilibrium ratios of the dimethylpentanes are not adequately known, but the similarity in results at 200 and 240° suggests that all four hydrocarbons appear in their equilibrium proportions. 3-Ethylpentane was not detected by infrared absorption. However, when gas chromatography became available, samples were reexamined and found to contain small amounts of 3-ethylpentane.[16] This hy-

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[15] A more accurate treatment of parallel racemization and isomerization is given in reference 4a, but a simpler treatment suffices here.

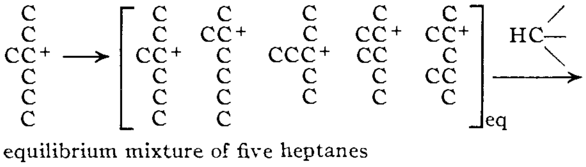
[16] Gas chromatographic examination of run 4A (Table I) gave an analysis consistent with that calculable from Table II but showed in addition about 0.6% of 3-ethylpentane and a few tenths % of cracked products. Similar results were obtained with run 12A (Table I). Such small quantities would have eluded infrared analysis.

drocarbon is strongly disfavored thermodynamically and the observed amounts of 3-ethylpentane were probably the equilibrium ones.

(2). Isomerization to hydrocarbons lacking a tertiary hydrogen atom can be better studied with methylcyclopentane in which thermodynamics permits but one isomer, cyclohexane, to be formed in any appreciable quantity. With sulfuric acid, less than 1% of cyclohexane was formed in a run of duration equivalent to 1.5 half-lives of isotopic exchange (ref. 4a, Table IV, run m). Similarly, in run 40A with silica–alumina (used catalyst, 0.05 cc. of D_2O, 20 hr., 200°) at one half-life of exchange, the product contained less than 1% cyclohexane as determined by catalytic dedeuteration over nickel followed by infrared analysis. Gas chromatography indicated the rate of formation of cyclohexane to be less than 0.01 that of isotopic exchange. However, in runs 41A and 42A (fresh catalyst, 0.1 cc. of H_2O, 67 hr., 170°), we obtained a 2% conversion of methylcyclopentane to cyclohexane and a 1% conversion of cyclohexane to methylcyclopentane, respectively. Because of the smaller amount of added water, runs 41A and 42A were much more drastic than 40A and corresponded to at least ten half-lives of "exchange." Thus, the rate of exchange is about 500 times that of isomerization.

(3). The formation $C_nD_{2n+1}H$ but not C_nD_{2n+2} accords with the results with deuterosulfuric acid.[17] The perdeuterocarbonium ion has no opportunity to abstract a deuteride ion in Step 2. Similar results have been reported for isobutane on silica–alumina catalyst.[11,13] Runs 29A, 26C (Fig. 1) and 39C (Table IV) show particularly clearly that this is also true for higher molecular weight alkanes. However, in runs with similar alkanes but with 70–95% of the molecules exchanged, Hindin, Mills and Oblad[12] report exchange of the tertiary hydrogen atom. At such high conversions, doubly branched species such as 2,3-dimethylbutane are formed and one of the tertiary hydrogen atoms can be deuterium. Transfer of this atom in Step 2 can form a perdeuteroalkane. Furthermore, at these high conversions, the isotopic distribution patterns approach the statistical.[12] At such high conversions, almost any mechanism would give this result. At low conversions, our patterns are much broader than the statistical (see run 27C, Fig. 1). The patterns of exchanged isobutane reported by Haldeman and Emmett[13] are also broader and our patterns resemble those they report for higher degrees of catalyst rehydration.

(4). At 200° and above, Step 2″, isomerization, must be assumed faster than Step 2, hydride ion transfer



equilibrium mixture of five heptanes

Since nearly every molecule must have traversed a necessarily optically inactive species such as the carbonium ion from 2-methylhexane, one must expect that the 3-methylhexane re-formed would be racemic.

With sulfuric acid-d_2, only those hydrogen atoms adjacent to a tertiary position can exchange.[17] However, at 200° on silica–alumina, the extensive isomerization should expose all hydrogen atoms in a carbonium ion to the possibility of exchange as is indeed, observed. Exact isotopic exchange patterns would depend in a rather complicated fashion upon relative rate constants in the isomerization processes, rate constants in exchange and hydride ion transfer and upon the rate of exchange between heavy water and those deuterium atoms on the surface which are involved in isotopic exchange.

Thus, at 200°, nearly every molecule which reacts would be both optically inactive and isotopically exchanged. As shown in Table III, this is true to within the available precision.

Isomerization and Loss of Rotation at Temperatures below 200°.—As shown in Table II, isomerization declines relative to loss in rotation at temperatures below 200°. With declining temperatures, the dimethylpentanes fall away first, then 2-methylhexane. By 56°, one deals with a nearly pure racemization. The products formed and the decline of isomerization with temperature resemble the results of the reaction between (+)3-methylhexane and sulfuric acid-d_2 and chlorosulfonic acid-d.[4,5] Table V presents k_R/k_i as a function of temperature for both systems. k_R and k_i are the rate constants for loss of rotation and isomerization, thus[5]

$$k_R/k_i = \ln(1 - \Delta\beta/\alpha_0)/\ln(1 - X_2/X_2^{eq})$$

where $\Delta\beta$ is the loss in rotation, α_0 is the original rotation, X_2 is the mole fraction of 2-methylhexane and X_2^{eq} is its value in an equilibrium mixture with 3-methylhexane. The quantity of water employed with the silica–alumina catalyst at −4 and 56° is much less than at the higher temperatures. One could hardly cover such a large range of temperature with a catalyst of constant activity. While the difference in water content might contribute to the decline in the relative rate of isomerization, the trend with temperature is already clearly visible in the results at higher temperatures.

TABLE V

VARIATION OF k_R/k_i WITH TEMPERATURE

Temp., °C.	Catalyst	k_R/k_i	Temp., °C.	Catalyst	k_R/k
60	96% H_2SO_4	1	240	$SiO_2 \cdot Al_2O_3$	1
30	100% H_2SO_4	1.4	200		1
0	$HClSO_3$–H_2SO_4	3.1	125		1.9
−33	$HClSO_3$	24	56[a]		15
−78	$HClSO_3$	51	56[b]		12
			−4[c]		15

[a] Run 22D. [b] Run 33D. [c] Run 35D.

Results at 120°.—Except for the decline in isomerization relative to loss in rotation, results at 120° are very similar to those at 200–240°, and, in particular: (1) degrees of exchange and loss in rotation are equal; (2) depths of exchange are large and nearly as large as at higher temperatures (compare run 32C, Table IV, with run 27C, Fig. 1).

As shown in comment 4 of Results at 200–240°, at 200° these results are a necessary consequence of

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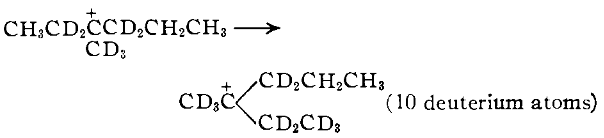
[17] D. P. Stevenson, C. D. Wagner, O. Beeck and J. W. Otvos, THIS JOURNAL, **74**, 3269 (1952).

equilibrium migration of methyl groups in the 2- and 3-methylhexane system. The equilibrium nature of the products at 200–240° is compatible with a number of possible variations in the basic mechanism and the extensive methyl group migration may well obscure the consequences of other processes.

The decline in relative degree of methyl group migration at 120° (Table II, run 21A), in fact, exposes another process since much 3-methylhexane must be re-formed without traversing the 2-methylhexane structure. Complete racemization of product 3-methylhexane cannot entirely result from all reacting species necessarily traversing the optically inactive 2-methylhexane structure, nor can one invoke mere isomerization to 4-methylhexane since this could hardly racemize all 3-methylhexane without leading to equilibrium formation of 2-methylhexane.

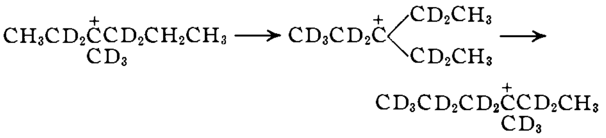
The observed degree of methyl group migration is also too little to account for the observed depth of exchange if one permits exchange of only those hydrogen atoms contiguous to the tertiary position. About 60% of the molecules which exchanged in run 32C appear as (±)3-methylhexane yet only 17% of the total molecules have seven or fewer deuterium atoms. Isomerization to 4-methylhexane would expose two more hydrogen atoms but nearly half of the (±)3-methylhexane is more exchanged than this. A similar situation seems to exist in run 30C at 140° (Table IV). This could support the belief of Hindin, Mills and Oblad[12] "that all primary and secondary atoms of the structure, *however far removed from the chain branch*, can exchange."

Their arguments for this conclusion, in essence similar to those above, consider migrations of methyl groups only. However, in sulfuric acid, 3-ethylpentane isomerizes unusually rapidly[17] and, here, an ethyl group must migrate. Thus, migrations of ethyl and propyl groups could be important and *both would lead only to 3-methylhexane with a rearranged carbon skeleton*. For a propyl group migration with exchange of contiguous hydrogen atoms only



If the absorbed carbonium ion retained the capability of optical activity, this process would probably involve inversion of configuration.

An ethyl group migration forms the 3-ethylpentane carbonium ion. Since 3-ethylpentane is thermodynamically disfavored and will not appear appreciably in the product, the ion can only suffer another ethyl group migration



If the original carbon atom again becomes the tertiary one, a maximum of nine deuterium atoms would be exchangeable, if one of the other two (original carbon atoms 2 or 5), twelve. Any product would be racemic since the intermediate carbonium ion is optically inactive. Since migration of ethyl and propyl groups can account both for racemization and extensive multiple exchange, we tentatively suggest that such migrations are as important at 120–240° as those of methyl groups. As will appear, one must assume that the relative rates of ethyl and propyl group migrations increase with temperature.

Results at 56 and −4°.—The essential results are: (1) loss in rotation exceeds exchange and very considerably exceeds isomerization (see run 22D, Table II and runs 33D-36D, Table III). (2) There are three products from runs with heavy water: (a) 3-methylhexane extensively multiply exchanged up to seven hydrogen atoms; (b) 2-Methylhexane more deeply exchanged than the 3-methylhexane; (c) Unexchanged but racemized 3-methylhexane. (3) In experiments at lower temperatures, adequate rates necessitated smaller quantities of water. Excessive isotopic dilution was partly counteracted in runs 33D and 35D by addition of deuteroisopentane. In these runs, unlike in runs 34D and 36D with light isopentane added, large quantities of 3-methylhexane-d_1 were formed (Table III, runs 33D-36D; Table IV, runs 33D and 36D). The alkane-d_1 results from abstraction of a deuterium atom from the tertiary position of deuteroisopentane and gives a measure of the extent of the hydride ion transfer reaction, Step 2. Forty per cent. of the tertiary hydrogen atoms in the mixture were deuterium. If an isotope effect of about 2.5 favors abstraction of "H^-" *vs.* "D^-", then the degrees of racemization are consistent with the assumption that all molecules racemized proceed as carbonium ions through Step 2.

The degree of reaction as measured by loss in rotation exceeds that of exchange (anomalous d_1 excluded) by a factor of two at 56° and by a factor of six (Table III) at −4°.

Furthermore, the isotopic exchange patterns show little exchange of 3-methylhexane beyond $C_7D_7H_9$ (runs 36D and 33D, Table IV). In these runs, the 2-methylhexane product is distinctly more deeply exchanged than the 3-methylhexane unlike run 32C at 120° where the 2-methylhexane had been but very slightly more deeply exchanged.[18] At the lowest temperatures, then, methyl group migration has become more important than ethyl and propyl group migration. One must assume that ethyl and propyl group migration declines with decreasing temperature more rapidly than methyl group migration.

Mechanism at 56 and −4°.—Products (a) and (b) of item (2) are those predicted from an extra-

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(18) The mass spectrometric peaks resulting from loss of a methyl radical (mass 85 and up) are largely derived from the content of 2-methylhexane since the sensitivity of this molecule much exceeds that of 3-methylhexane at this peak. One can roughly correct for the contribution of deuterated 3-methylhexane to the hexyl carbonium ion peaks and derive the approximate 2-methylhexane pattern. In run 33D at 56° the most abundant hexylcarbonium ion derived from 2-methylhexane is $C_6H_8D_5^+$ and species up to $C_6H_3D_{10}^+$ are detectable. Runs 35D (Table III) and 36D (Table IV) gave very similar results. The quantities of 2-methylhexane so found check those reported in Table III.

polation of behavior at higher temperatures assuming that the ratio of hydride ion transfer (Step 2) to isomerization (Step 2") continues to increase with decreasing temperature. However, a problem appears in the juxtaposition of products (a) and (c), rather large quantities of unexchanged 3-methylhexane with rather extensively exchanged 3-methylhexane. Many mechanisms would predict major formation of material of degrees of exchange intermediate to these extremes. One needs either different sites for the formation of product (c) or a mechanism in which isomerization and isotopic exchange occur in a state separated by an activation energy barrier from that of the carbonium ion involved in hydride ion transfer. The carbonium ion involved in Steps 2′ and 2″ might be of a more extreme carbonium ion type and located on sites different from those involved in Step 2 or, less likely, on the same sites but with different separation from the surface. In homogeneous systems different types of carbonium ions (intimate ion pairs, solvent separated ion pairs and dissociated ions) have been proposed[19] and originally they were proposed for a similar reason, excess racemization.

In reaction in sulfuric acid we have assumed[4] that the carbonium ion from (+)3-methylhexane is necessarily optically inactive since it appears likely that the ion would be planar and symmetrically solvated. Adsorbed on a surface, however, the carbonium ion is not necessarily racemic.[20] Its racemization requires either: (a) transition through a symmetric adsorbed intermediate, or (b) a turning over of the plane of the carbonium ion. Process (b) would involve substantial separation of the carbonium ion from the surface against the forces holding it to the surface. We believe these forces to be large and such a process to be difficult, since the energy of interaction of a carbonium ion with the surface must approach the energy of solvation of the ion in media such as sulfuric acid, many tens of kilocalories.

It has recently been reported[21,22] that a silica–alumina catalyst of a composition similar to the one which we have studied consists of a loosely packed aggregate of spheroids, which are about 46 Å. in diameter and of which there are about 10^{19} per gram. If each spheroid touches eight others, there are 0.07 mole of junctions between spheroids per gram. The number of acid sites per gram of silica–alumina catalysts is about five times this number.[23] The roughly, V-shaped, annular intersections of these spheroids are of interest as catalytic sites. They provide the possibility of "solvating" both sides of a carbonium ion or the acid form of an indicator. This would make the energetics of ion formation more favorable than mere adsorption of ions on a planar surface. In addition, such adsorption might well permit the ion to become racemic.[24]

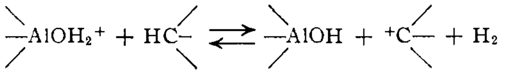
The stereochemical requirements of Step 2, hydride ion transfer, have been little discussed. Both the original carbonium ion and the alkane molecule becoming a carbonium ion must be so located that they can strongly interact with the surface and yet the two tertiary carbon atoms and the "hydride ion" must lie in a straight line. It is difficult to see how this can occur on a planar surface, although it might be possible in a crevice. Alternatively, and rather more simply geometrically, surface or slightly subsurface sites may serve as storage depots for "hydride ions" such that Step 2 occurs in two stages, abstraction of a hydride ion from the surface by a carbonium ion with subsequent donation of a hydride ion to the site by another alkane. Such a process is related to one of the possibilities of chain initiation discussed in the next section.

In summary, the following tentative proposal correlates the data. Crevice sites are involved in at least some of the reaction stages. There are two types of sites A and B, the latter involving more extreme carbonium ion character. Migration from A to B involves an activation energy. Either or both of the sites could be regions rather than points. Hydride ion transfer occurs on sites A, isomerization and isotopic exchange on sites B.[25] At lower temperatures isomerization on sites B involves primarily methyl group migration but at higher temperatures, ethyl and propyl migration become important. If sites B are rather substantial regions of the surface over which carbonium ions could freely migrate, the carbonium ion would have available the large exchange pool of deuterium which is required for the extensive isotopic exchange which is found.[12,13]

Chain Initiation.—The origin of the carbonium ion chain carrier has been in controversy.[26] Proposed origins have involved (a) reaction of impurities, *e.g.*, the addition of a proton from a Brønsted acid site to an olefinic impurity and (b) oxidation of a tertiary hydrocarbon to a carbonium ion or a carbonium ion precursor such as an olefin.

A subclass of category (b) consists of reactions which involve formation of hydrogen in equilibrium with the reactant hydrocarbon. Examples are

$$\text{alkane} \rightleftarrows \text{olefin} + H_2 \qquad (4)$$


(5)

$$\text{—AlOH}_2{}^+ + \text{HC—} \rightleftarrows \text{—AlOH} + {}^+\text{C—} + H_2 \qquad (5)$$

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[19] S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, THIS JOURNAL, **78**, 328 (1956).

[20] This stereochemical problem is discussed, R. L. Burwell, Jr., *Chem. Revs.*, **57**, 915 (1957).

[21] W. G. Schlaffer, C. Z. Morgan and J. N. Wilson, *J. Phys. Chem.*, **61**, 714 (1957).

[22] C. R. Adams and H. H. Voge, *ibid.*, **61**, 722 (1957).

[23] H. A. Benesi, *ibid.*, **61**, 970 (1957).

[24] A number but not all possible types of crevice sites would lead to racemization. We do not see how to select from among the possibilities. For example, interaction within a crevice would permit the plane of the carbonium ion to turn over much more easily than upon a planar surface. Or, in a crevice site, the hydride ion might be removed from one side to form the carbonium ion but added to the opposite side. Certain kinds of surface mobility would also permit racemization.

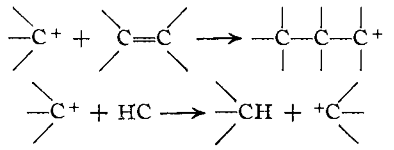
[25] Alternatively, hydride ion transfer could occur on both sites but isomerization and exchange only on B. We have been able to think of only one way in which sites A could avoid being cevice sites. In either model above, isomerization might also occur on sites A but only that isomerization resulting from the shift of ethyl and propyl groups while the isomerization on site B would involve primarily methyl group migration. Site A would then produce racemic but unexchanged 3-methylhexane. This model appears unlikely but it could be tested by isotopic labelling of the carbon skeleton of 3-methylhexane.

[26] V. Haensel, "Advances in Catalysis," Vol. III, Academic Press, Inc., New York, N. Y., 1951, p. 186. A. G. Oblad, T. H. Milliken, Jr., and G. A. Mills, *ibid.*, Vol. III, 1951, p. 239. R. C. Hansford, *ibid.*, Vol. IV, 1952, p. 21.

The equilibrium constant for (4) is very unfavorable to olefin but one might need but a very small amount in a chain reaction. Furthermore, adsorption of olefin or its conversion to a carbonium ion might shift the equilibrium to the right as compared with the vapor phase. Since loss or rotation of (+)3-methylhexane provides a simple method of rate measurement, using apparatus C we compared losses of rotation in the presence of 25 mole % nitrogen with that with 25 mole % hydrogen. If reactions such as (4) or (5) are in equilibrium, replacement of nitrogen by hydrogen should depress the concentration of carbonium ion by a factor of about 1000. In fact, the reduction in rate was small or zero. Therefore, the chain initiation step cannot involve the *equilibrium* formation of hydrogen. Non-equilibrium formation of hydrogen is not excluded.

The impurity usually considered in category (a) is olefin. One set of workers[10] has reported that added isobutylene increases rates of isotopic exchange of isobutane substantially, another set reports only a small increase.[11] We have tested the effect of 0.4 to 3.7 mole % of 2-methyl-1-hexene upon the rate of loss of rotation of (+)3-methylhexane (Table I, runs 2A, 14A, 15A and 16A). Our results round out the possibilities, olefin decreases rates. We dealt with an olefin which probably undergoes polymerization and conjunct polymerization rather readily. The olefin was completely adsorbed on the lowest sections of the catalyst with darkening during the first cycle. The observed degrees of loss of rotation were about proportional to the undarkened portions of the catalyst.

Actually, these results are not very diagnostic as was somewhat the case with similar experiments in sulfuric acid[4b,16] and for similar reasons. Alkane and olefin will compete for carbonium ions



If olefin is the carbonium ion precursor, the first reaction is second order in olefin, the second, first order. Intrinsically, the first reaction is also much faster. Thus, olefin is rapidly removed from the gas phase and, in runs 14A, 15A and 16A of Table I, with deactivation of catalyst. One must expect the effect of olefin on reactions on silica-alumina catalysts to vary with the polymerizability of the olefin and with the method of introduction of olefin which was different in the three described investigations.

Our experiments do not exclude the possibility that small amounts of olefin are the chain initiators. Judging from adsorption and catalyst discoloration, our (+)3-methylhexane contained less than 0.01% olefin.

The Effect of Water.—Previous work establishes that, as one adds H_2O or D_2O to a dehydrated silica-alumina catalyst, catalytic activity for exchange or isomerization increases from zero to a maximum and then declines.[9,13,14] In our sealed tube experiments (apparatus D) we worked near that maximum, 0.1% added water. However, in the recycle apparatus (A and B) we worked with 20 or 100 times that amount (0.1 and 0.5 cc. per 10 g. of catalyst). This rather large amount of water suppresses the cracking which is observed at 150° with the optimum amount.[12,14]

The 0.1 cc. of water was absorbed by the catalyst and no recycle of water was observed but most of the 0.5 cc. recycled. During any one run, catalyst activity rose from zero to a maximum and then declined. With 0.5 cc. of water, the activity declined to zero since degrees of conversion were not increased by extensive prolongation of runs (see runs 10A and 11A in Table I) and at 200°, for instance, it was impossible to obtain losses in rotation exceeding 15%. However, such catalysts could be regenerated for runs employing 0.5 cc. of water merely by evacuation at room temperatures for 1 hr. One catalyst was carried through a sequence of eight such runs at 160–240° without detectable change in activity.

As shown by runs 1A–5A in Table I, with 0.1 cc. of water, activity declined with time but not to zero. Evacuation of the catalyst at room temperatures did not restore the original activity completely but evacuation for 4 hr. at 450° did.

The runs at higher temperatures in Table III show excellent agreement between loss in rotation and fraction of alkane molecules exchanged. In these runs, the catalyst had been used previously in a run with D_2O. In two runs with fresh catalyst and 0.1 cc. of D_2O, no isotopic exchange could be detected (200°, 4 hr., 55% loss in rotation; 160°, 2 hr., 23% loss). In runs with fresh catalyst and 0.5 cc. of D_2O, isotopic exchange occurred but to a lesser degree than loss of rotation. In a 24-hr. run at 160°, the loss in rotation was 7.4%, the fraction of molecules exchanged, 2.6%. However, the isotopic exchange pattern was normal and resembled that of run 29A, Fig. 1. Run 38A in Table IV is also normal (200°, 0.5 cc. of D_2O, 3 hr., 2,4-dimethylpentane). A similar run on 2,3-dimethylbutane also gave a normal distribution pattern. All of the runs mentioned in this paragraph were on Apparatus A.

Under somewhat different conditions, the exchange between deuterium atoms of added heavy water and those already on the catalyst is more rapid.[27] The origin of this seeming anomaly is not clear and further study of the reaction on our system would be desirable. For the purposes of the present paper, we merely attempted to avoid the conditions described in the preceding paragraph once the phenomenon had been observed.

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EVANSTON, ILLINOIS

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(27) R. G. Haldeman and P. H. Emmett, THIS JOURNAL, **78**, 2917 (1956).