

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY

**The Action of 96% Sulfuric Acid on Alkanes at 60°<sup>1</sup>**

BY ROBERT L. BURWELL, JR., ROBERT B. SCOTT, LUCIEN G. MAURY AND ALLEN S. HUSSEY

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Agitation with sulfuric acid results in relatively rapid interconversion of methylhexanes and of methylheptanes. Isomerization to dimethylpentanes and to dimethylhexanes occurs more slowly. Quantitative data relative to isomerization, racemization of (+)3-methylhexane and (+)3-methylheptane, isotopic exchange with D<sub>2</sub>SO<sub>4</sub>, and chain length are interpreted in terms of an extension of a previous mechanism.<sup>2</sup> Chain initiation occurs by oxidation of an alkane at the tertiary position to form a carbonium ion or its equivalent. The carbonium ion chain carriers come to equilibrium in regard to simple methyl-shift and isotopic exchange before abstracting hydride ions from tertiary positions of alkanes to produce alkanes and new chain carriers. The degree of agitation affects absolute rates but not relative rates of loss in rotation, isomerization and isotopic exchange.

Previous work at this Laboratory has dealt primarily with the interrelation of isotopic exchange and loss of rotation in the action of sulfuric acid-d<sub>2</sub> on hydrocarbons of the type of (+)3-methylhexane.<sup>2</sup> This paper reports an extension of these studies on the action of sulfuric acid on alkanes at 60°. The action of sulfuric acid at lower temperatures and of halosulfonic acids is reported separately.

**Experimental Techniques**

**Materials.**—The preparation of (+)3-methylhexane and (+)3-methylheptane has been described.<sup>2</sup> The olefin intermediate in the case of the first compound required fractionation in a 150-plate Podbielniak Heligrad column.

2-Methylhexane was prepared by coupling the Grignard reagent of isobutyl bromide with allyl bromide and hydrogenating the resultant olefin. (±)3-Methylhexane was similarly prepared by coupling the Grignard reagent of allyl bromide with *s*-butyl bromide. A much poorer yield resulted from coupling the Grignard reagent of *s*-butyl bromide with allyl bromide. 2-Methylheptane was prepared from the Grignard reagent of isoamyl chloride by coupling with allyl bromide. 4-Methylheptane was prepared by adding ethyl acetate to the Grignard reagent of propyl bromide, and dehydrating the resultant 4-methyl-4-heptanol over alumina (Harshaw Puralox) at 350°. All olefins were hydrogenated with nickel-kieselguhr and hydrogen at 125 atmospheres at 70°.

Following hydrogenation, the hydrocarbons were extracted at 0° with concentrated sulfuric acid, fractionated in columns of at least 50-theoretical plates and stored over potassium metal. The infrared absorption spectra of these hydrocarbons were compared with those of Bureau of Standards standard samples by a substitution method at a large number of wave lengths. Negligible difference was found. However, the presence of traces of olefins cannot be excluded since, in general, absorption in the ultraviolet started at about 2200 Å. In later experiments, treatment with sulfuric acid was replaced by silica gel percolation.

3,3-Dimethylhexane, reported to be 99.1 ± 0.3 mole % pure, was supplied by A. P. I. Research Project 45 at the Ohio State University.

One batch of sulfuric acid was employed, 96.04 weight % by titration.

**Experimental Procedures.**—Initially, reaction mixtures were assembled by high vacuum techniques and run under purified nitrogen as previously described.<sup>2</sup> After it had been established that the presence of oxygen was without effect, runs were made without these precautions. In the runs in which successive samples were analyzed for isomerization, stirring was interrupted and a small sample of the hydrocarbon layer was pipetted out. Stirring was then restarted.

Magnetic stirring was employed. In experiments employing vacuum techniques, an Erlenmeyer-like flask with a flat bottom was provided with a stirring bar of semi-circular

cross-section. This gave better stirring than the round-bottomed flask used before.<sup>2</sup> This type of stirring when run at maximum speed is called *standard*.

Certain experiments were run in a round-bottom tube 15 mm. in diameter at the bottom of which was placed a glass-encased stirring bar of such length that it leaned at an angle of about 30°. This procedure gave an emulsion which took several times as long to break as the one resulting from standard stirring. This stirring procedure will be designated as *rapid*. Runs with *rapid* stirring were in air.

In the experiments with *standard* stirring, 3.25 cc. of hydrocarbon and 4.5 cc. of sulfuric acid were employed unless otherwise stated. A similar ratio was employed with *rapid* stirring using about 1.2 cc. of hydrocarbon. All runs were at 60°.

**Infrared Absorption Analysis.**—A Beckman IR2 was employed using a closely matched cell pair. In isomerizations of 3-methylhexane, that hydrocarbon was always placed in cell A, the product of a run, in cell B. The ratio of transmissions of the two cells was obtained as a function of the ratio of 3- to 2-methylhexane for a series of synthetic mixtures of known compositions at 7.43, 8.63, 10.43, 11.09 and 12.98 μ. These wave lengths correspond to extrema in the ratio of transmissions of the two hydrocarbons, which extrema are independent of the ratio of amounts of the two hydrocarbons.

The composition of an unknown was determined by reference to a plot of the logarithm of the transmission ratio against % 2-methylhexane. The plots at the two smaller wave lengths deviated seriously from Beer's law. Synthetic mixtures could be analyzed to ±0.1% with results at all five wave lengths agreeing. Products of isomerization runs gave a greater spread because of the presence of other substances, particularly dimethylpentanes.

Accuracy of analysis was checked in selected cases by preparing a synthetic mixture of composition corresponding to the analysis and employing this in cell A. Transmission ratios were measured with the synthetic mixture in cell B and then with the experimental product in the cell over a wide range of wave lengths at close intervals. Purity of hydrocarbons was checked similarly.

2,3- and 2,4-dimethylpentanes in 2- and 3-methylhexane were determined by measurement at wave lengths at which 2- and 3-methylhexane had identical absorption. Coefficients of absorption of the two dimethylpentanes were determined at these wave lengths from synthetic mixtures in 3-methylhexane. Beer's law was assumed valid.

In the case of methylheptane isomerizations, the absorption of each of the methylheptanes and of 2,3-, 2,4-, 2,5- and 3,4-dimethylhexane was determined against a carbon disulfide-filled cell. Measurement was made at wave lengths at which two methylheptanes had identical absorption. The results are of lower precision than in the heptane system.

**Mass Spectroscopy.**—Analysis was performed by the Analytical Service Laboratory of the Consolidated Engineering Corporation of Pasadena, California.

**Experimental Results**

**Effect of Oxygen and Effect of Stirring.**—Table I presents data on loss of rotation and of isomerization of (+)3-methylhexane as a function of stirring and of the presence of oxygen. The presence of dimethylpentanes was ignored in the isomeriza-

(1) Presented at the Gordon Research Conference on Petroleum, June, 1951.

(2) (a) R. L. Burwell, Jr., and G. S. Gordon, III, *THIS JOURNAL*, **70**, 3128 (1948); (b) G. S. Gordon and R. L. Burwell, *ibid.*, **71**, 2355 (1949).

tion analysis but this is of no consequence to the comparative correlations derived.

TABLE I  
ISOMERIZATION AND RACEMIZATION OF (+)3-METHYLHEXANE BY SULFURIC ACID AT 60° IN TWO HOURS, STANDARD STIRRING

Run	Atmosphere	Relative rate of stirring <sup>a</sup>	$\Delta\beta/\alpha_0, f$ %	2MH, %	$\Delta\alpha/\alpha_0, f$ %
a	Pure N <sub>2</sub>	1.00	31.8	21.2	13.4
b	Pure O <sub>2</sub>	1.00	31.0	22.4	11.1
c	Dry tank N <sub>2</sub>	1.00	32.5	23.2	12.1
d	Pure N <sub>2</sub>	0.94	30.8	20.7	12.8
e	Pure N <sub>2</sub>	.85	30.3	19.1	13.8
f	Dry tank N <sub>2</sub>	.63	28.8	19.1	12.0
g	Pure N <sub>2</sub>	.08	25.4	18.8	8.2
h	Pure N <sub>2</sub>	<sup>b</sup>	14.5	..	..
i	Pure N <sub>2</sub>	None	1.5	..	..
j	Air	None <sup>c</sup>	21.9	14.2	8.9
k	Air	1.00 <sup>d</sup>	55.7	..	..
m	Air	<sup>d,e</sup>	57.3	31.7	37.3

<sup>a</sup> Relative rate at which stirring bar was turned. <sup>b</sup> Stirring bar was just kept moving. <sup>c</sup> Placed in oven in glass capped flask for 112.3 hours. <sup>d</sup> Twice customary ratio of acid to hydrocarbon. <sup>e</sup> Rapid stirring. <sup>f</sup>  $\beta$  is the observed rotation.  $\alpha$  is the rotation which (+)3-methylhexane would have if isolated from the reaction mixture.  $\alpha_0 \equiv \beta_0$ .

**Products of Isomerization of 2- and 3-Methylhexane.**—Results of runs on these two hydrocarbons are presented in Table II. Mass spectroscopic and infrared analysis check reasonably well. The infrared analyses in Run I illustrate the degree of error involved in ignoring dimethylpentanes.

TABLE II  
ISOMERIZATION OF METHYLHEXANES BY SULFURIC ACID AT 60°<sup>a</sup>

Run no.	Time, min.	$\Delta\beta/\alpha_0, f$ %	Analysis <sup>b</sup>	Methylhexanes, % 2- 3-	Dimethylpentanes, % 2,3- 2,4-
2-Methylhexane <sup>d</sup>					
1	30		IR <sup>c</sup>	95.0 5.0	
			MS	92.7 6.0	Nil 1.3
	60		IR <sup>c</sup>	85.4 14.6	
			MS	84.1 13.5	1.1 1.3
3-Methylhexane <sup>d</sup>					
2	30	16.7	MS	8.9 88.2	0.8 1.1
	60	32.4	MS	17.7 79.8	1.5 1.0
	120 <sup>e</sup>	59.4	IR	32.0 61.8	3.0 3.1
			MS	30.7 62.9	1.8 4.6
	300	82.0	IR	47.0 41.1	6.6 5.2
			MS	41.0 48.3	4.3 6.4

<sup>a</sup> Run with successive removal of samples at times indicated. <sup>b</sup> IR, analysis by infrared; MS, by mass spectroscopy. <sup>c</sup> These analyses were computed assuming that 3-methylhexane was the only product. <sup>d</sup> Twice the usual ratio of sulfuric acid to hydrocarbon was employed. <sup>e</sup> The acid was replaced with fresh acid after the 120-min. sample was removed. <sup>f</sup>  $\Delta\beta/\alpha_0$  is the fractional loss of rotation.

**Isomerization of 2-, 3- and 4-Methylheptane.**—Table III presents results of isomerization of methylheptanes. Preliminary infrared analysis of the result of protracted isomerization of 4-methylheptane indicated that the infrared absorption curve could be reasonably well interpreted in terms of the five-component system: 2-, 3- and 4-methylheptane and 2,4- and 2,5-dimethylhexane.

No evidence for the presence of 2,3- and 3,4-dimethylhexane could be found. Other infrared analyses were computed on the assumption that only the five materials listed were present.

TABLE III  
ISOMERIZATION OF METHYLHEPTANES AT 60°

Run no.	Time, min.	$\Delta\beta/\alpha_0, f$ %	Analysis <sup>b</sup>	Methylheptanes, % 2- 3- 4-	Dimethylhexanes, % 2,4- 2,5-
2-Methylheptane					
3	30	..	IR	83.8 4.1 3.2	4.5 4.4
			IR	82.8 5.9 3.2	2.5 5.7
	60		IR	73.0 6.7 5.7	8.7 5.9
	180		IR	50.1 17.2 9.5	11.9 11.3
(+)3-Methylheptane					
4	60	15.7	MS	4.3 87.9 3.9	.. 3.9
	300	27.0	IR	11.7 81.4 3.3	2.4 1.2
			MS	9.1 80.6 5.1	.. 5.2
	5 <sup>c</sup> 180	36.4	IR	15.8 71.1 5.0	5.9 2.3
	6 <sup>c</sup> 30	18.5	IR	8.9 81.7 3.3	6.3 -0.2
			IR	11.0 80.0 1.6	10.4 -3.0
			MS	4.9 84.0 3.6	2.2 2.8
			IR	7.7 82.1 4.7	5.9 -0.4
	60	23.3	IR	11.4 78.0 3.7	6.4 0.5
			MS	6.9 83.3 4.1	.. 3.4
	182	36.1	IR	15.8 71.1 5.0	5.9 2.3
			MS	11.8 71.4 5.3	3.6 5.3
4-Methylheptane					
7 <sup>c</sup>	30	..	IR	5.8 3.8 84.1	3.0 3.3
			MS	10.1 3.4 84.1	.. ..
	60	..	IR	9.2 9.4 71.7	3.1 6.6
			MS	14.7 7.4 70.9	3.9 ..
	120	..	IR	17.0 14.4 52.2	6.6 9.8
			MS	21.8 13.7 52.9	6.2 1.9
	240 <sup>d</sup>	..	IR	24.5 22.6 31.9	8.8 12.2
	480	..	IR	28.3 19.8 16.0	18.6 17.3
			IR	26.3 23.8 16.5	14.6 18.8

<sup>a</sup> The infrared analysis of a synthetic sample of the composition given on the preceding line. <sup>b</sup> Analysis: IR, infrared; MS, mass spectroscopy. <sup>c</sup> Double the usual ratio of acid to hydrocarbon. <sup>d</sup> After removing this sample, the sulfuric acid was replaced by fresh acid.

The analysis of the synthetic sample (second line, run 3) confirms the validity of the analytical procedure. The ratio of absorptions of the synthetic and experimental samples was determined over a variety of wave lengths as described under Infrared Absorption Analysis. Some departure from unity was observed at some wave lengths. Since it appeared impossible to vary the concentrations of any of the five listed components so as to bring all departures from unity to zero, the presence of minor amounts of other substances is indicated.

Mass spectroscopic analysis indicated the presence of disproportionation in most cases in degree increasing with time of reaction. Where pentanes, hexanes and heptanes were present, higher molecular weight material also was found. As a typical case, in run 7, Table III, at 120 min., the mole % pentanes was 1.0; hexanes 0.8; and heptanes, 1.7. The presence of such disproportionation products reduced the accuracy of the mass spectroscopic analysis and in the 240 and 480 minute runs of run 7 made analysis impossible. Even in the latter case, however, the infrared analysis seems to have

at least semi-quantitative significance. Disproportionation was reported for methylhexanes in a few cases but in much smaller extent. No pentanes or hexanes were detected.

In run 9, 4-methylheptane was treated with double the usual ratio of acid for four hours and the hydrocarbon fraction was distilled in a Piro-Glover micro-distillation column. Successive fractions of 0.35, 0.34, 0.90 and 5.15 cc. were collected and analyzed mass-spectroscopically. Pentanes, hexanes and heptanes were reported in the first two fractions in quantities which would not permit the analysis of the octanes. The over-all analysis in mole % is

Pentanes	0.28	4-Methylheptane	47.3
Hexanes	0.13	2,3-Dimethylhexane	2.6
Heptanes	0.03	2,4-Dimethylhexane	1.6
2-Methylheptane	20.0	2,5-Dimethylhexane	2.8
3-Methylheptane	14.7	3,4-Dimethylhexane	0.2
		Total	89.6

Unanalyzed bottoms amounted to 0.7% and unidentified octanes in the first two fractions to 9.7%. 2,4- and 2,5-dimethylhexanes and any trimethylpentanes would be concentrated in the unidentified fractions. Distribution of the octanes in the fractions was consistent with their boiling points.

### Discussion

Simultaneous racemization, isotopic exchange and isomerization occur when (+)3-methylhexane or (+)3-methylheptane is treated with deuteriosulfuric acid.<sup>2</sup> Largely on the basis of correlation of loss of rotation and of exchange, it was proposed<sup>2</sup> that all three reactions occur by a chain reaction involving: (a) chain initiation by oxidation of the hydrocarbon by sulfuric acid to material in the oxidation state of olefin; (b) isomerization and isotopic exchange of the chain carrier (which is assumed optically inactive or racemic); (c) reaction between chain carrier and alkane to produce racemized, isomerized and exchanged alkane and new chain carrier; (d) chain termination by reaction of the chain carrier to form material which appears in the sulfuric acid layer.

Hydride ion transfer as in step (c) was first proposed by Bartlett, Condon and Schneider.<sup>3</sup>

The chain carrier has the behavior expected of a carbonium ion and will be so represented although exact specification of the nature of the chain carrier is not necessary for the application of the mechanism.

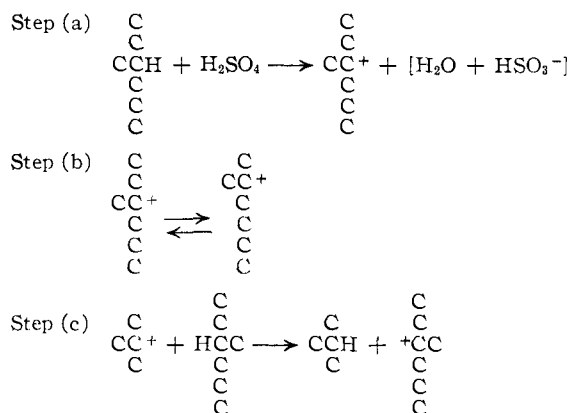
Otvos, Stevenson, Wagner and Beeck derived a similar mechanism from their elegant isotopic exchange experiments.<sup>4</sup>

This paper reports results of the action of 96% sulfuric acid at 60° on methylhexanes and on methylheptanes. Conclusions will be presented first in terms of methylhexanes.

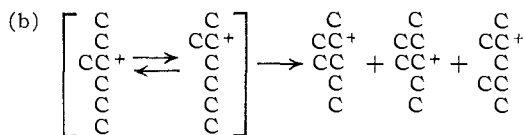
As applied to optically active 3-methylhexane the mechanism previously proposed takes the form

(3) P. D. Bartlett, F. E. Condon and A. Schneider, *THIS JOURNAL*, **66**, 1531 (1944).

(4) (a) J. W. Otvos, D. P. Stevenson, C. D. Wagner and O. Beeck, *ibid.*, **73**, 5741 (1951); (b) D. P. Stevenson, C. D. Wagner, O. Beeck and J. W. Otvos, *ibid.*, **74**, 3269 (1952).



In addition to the rapid simple methyl shift (step b) which was first observed,<sup>2</sup> there are slower isomerizations leading to changes in the degree of chain branching<sup>4b,5,6</sup> which in the present case would correspond to formation of 2,3- and 2,4-dimethylpentanes. Step (b), therefore, needs to be elaborated



The research reported in this paper was aimed at extending the mechanism first described particularly in regard to determination of the relative rates of steps (b) and (c), of the relative rates of the various types of isomerization, and of effect of hydrocarbon on step (a), chain initiation.

In using (+)3-methylhexane, the loss in rotation is a measure of the total hydrocarbon issuing from step (c) on the assumption that all species which have proceeded through a carbonium ion stage are racemic (3-methylhexane, 2,3-dimethylpentane) or inactive (2-methylhexane, 2,4-dimethylpentane). The degrees of isomerization are determined on samples of known loss of rotation. By difference, one may determine the fraction of 3-methylhexane in the hydrocarbon issuing from step (c).

As will be shown, at 60° with 96% sulfuric acid, 2- and 3-methylhexane appeared in the product in their equilibrium ratio. At this temperature, the equilibrium mole fraction of 2-methylhexane in a mixture of 2- and 3-methylhexane is 0.595.<sup>7</sup>

Under these conditions about 8% of all hydrocarbon issuing from step (c) consists of 2,3- and 2,4-dimethylpentane (runs 1 and 2, Table II) which appear in their equilibrium ratio, 4/6,<sup>7</sup> to within the precision of the data, which is low owing to the small amounts of dimethylpentanes present.

The absolute rates of the isomerization, loss in rotation and isotopic exchange reactions (when using sulfuric acid-*d*<sub>2</sub>) depend upon the degree of stirring in the heterogeneous system, acid-hydrocarbon. With the poorer stirring used before<sup>2</sup> and in the earlier parts of this research, it was difficult

(5) A. K. Roebuck and B. L. Evering, *ibid.*, **75**, 1631 (1953).

(6) K. N. Campbell and W. E. Erner, private communication.

(7) L. G. Maury, R. L. Burwell, Jr., and R. H. Tuxworth, *THIS JOURNAL*, **76**, 5831 (1954).

to reproduce rates to better than about 10 to 15%. Attention was focussed, therefore, upon the relative extents of loss of rotation and of isomerization in the same sample since this frees one from dependence upon reproducibility in rate.<sup>2</sup> However, it became possible under conditions of better stirring to duplicate runs to within better than  $\pm 2.5\%$  in rate so that certain conclusions could be drawn from absolute rates. As will be shown later, Table IV demonstrates that members of a set of simple methyl shift isomers, such as 2- and 3-methylhexane, undergo exchange at substantially the same rate.

TABLE IV

EXCHANGE OF HYDROCARBONS WITH D<sub>2</sub>SO<sub>4</sub> AT 60°, ONE HOUR<sup>a</sup>

Run	Hydrocarbon	Stirring <sup>b</sup>	Acid concn., %	D <sub>heq</sub>	D <sub>h</sub>	$k \times 10^3$ , sec. <sup>-1</sup>
a	2,2,3-Trimethylbutane <sup>f</sup>	Stand.	95.5	0.253	0.033	1.03
c	2-Methylhexane			.296	.125	4.94
d	3-Methylhexane <sup>c</sup>			.297	.129	5.01
e	3,3-Dimethylhexane			.320	.002	0.1
f	4-Methylheptane	Rapid	95.8	.336	.146	5.62
g	3-Methylheptane	<sup>d</sup>		.339	.078	2.73
h	3-Methylheptane <sup>e</sup>	Rapid		.342	.153	5.94
i	2-Methylheptane			.343	.150	5.58
j	2,3-Dimethylpentane			.375	.179	7.21
k	2,4-Dimethylpentane			.377	.180	7.25
m	Methylcyclopentane <sup>f</sup>			.380	.134	5.06
n	2,4-Dimethylpentane			.331	.162	6.58
o	3-Methylheptane			.341	.133	4.94
p	3-Methylhexane			.338	.126	4.65

<sup>a</sup> D<sub>h</sub> is fraction of hydrogen atoms in alkane product which are deuterium and D<sub>h</sub><sup>eq</sup> is that fraction which would obtain at equilibrium. <sup>b</sup> Standard and rapid stirring have been described under Experimental Procedures. <sup>c</sup>  $\Delta\beta/\alpha_0 = 0.179$ . <sup>d</sup> Stirring by rapid technique but at half speed.  $\Delta\beta/\alpha_0 = 0.097$ . <sup>e</sup>  $\Delta\beta/\alpha_0 = 0.206$ . <sup>f</sup> The infrared absorption spectra of these hydrocarbons were unchanged after stirring with sulfuric acid for 3 hr. This confirms for methylcyclopentane under more drastic conditions the lack of isomerization to cyclohexane previously reported.<sup>4b</sup>

With the best stirring, runs in which aliquots of emulsion were removed periodically for analysis showed that loss of rotation followed a first-order rate law to beyond 60% loss of rotation. In the same region, isomerization was a first-order reversible reaction. With poorer stirring, rate constants fell off with increasing conversions.

**Mechanism.**—These results suggest: (1) rates of chain initiation (step (a)) are the same for all of a set of methyl shift isomers, (2) carbonium ions at 60° come to equilibrium in simple methyl shift before hydride ion transfer occurs, and (3) hydride ion transfer from any of a set of methyl shift isomers is equally likely as in (1). The assumption under (2) becomes decreasingly valid as the temperature is lowered below 60°.<sup>8</sup>

On these assumptions, the rate of chain initiation in mole fraction units is  $k'$  for a particular ratio of hydrocarbon to acid. If  $c$  be the chain length,  $k'/c = k$ , which when corrected for concentration changes and reverse reaction gives the rates of loss of rotation, of isomerization and of isotopic exchange. When the quantity of dimethylpentanes is small enough to ignore their reverse isomerization to methylhexanes

(8) R. L. Burwell, Jr., L. G. Maury and Robert B. Scott, THIS JOURNAL, **76**, 5828 (1954).

$$-dX_3/dt = q(kX_2^{eq}X_3 - kX_3^{eq}X_2) + (1-q)kX_3 - k(X_3 - qX_3^{eq}M) \quad (1)$$

where,  $X_2$  and  $X_3$  are the mole fractions of 2- and 3-methylhexane,  $X_2^{eq}$  and  $X_3^{eq}$  are the equilibrium mole fractions of the two in a mixture of 2- and 3-methylhexanes only,  $M = X_2 + X_3$  (i.e.,  $1 - M$  is the mole fraction of dimethylpentanes) and  $1 - q$  is the fraction of carbonium ions which isomerize to ions derived from dimethylpentanes before step (c). Also

$$-dM/dt = (1-q)kM \text{ or } \ln M_0/M = (1-q)kt \quad (2)$$

From (1) and (2)

$$dX_3/dM = (1/(1-q))(X_3/M - qX_3^{eq}) \quad (3)$$

The change in rotation is

$$(\beta + d\beta)/\beta = (X_3 - kX_3 dt)/X_3 \text{ or } d\beta/\beta = -k dt$$

Whence, if one starts with pure 3-methylhexane

$$\ln(\alpha_0/\beta) = kt \text{ or } \ln(1 - \Delta\beta/\alpha_0) = -kt \quad (4)$$

$\beta$  is the actual rotation of product (partially racemized 3-methylhexane plus isomers) and  $\alpha$  would be the rotation of isolated 3-methylhexane,  $\beta/X_3 = \alpha$ .  $\Delta\beta/\alpha_0$  is the fractional loss in rotation.

Integrating equation 3 starting with pure 3-methylhexane, and employing equations 2 and 4

$$\ln \frac{X_3/M - X_3^{eq}}{1 - X_3^{eq}} = \frac{q}{1-q} \ln M = q \ln(1 - \Delta\beta/\alpha_0) = qkt \quad (5)$$

Whence

$$1 - (1 - X_2/X_2^{eq}M)^{1/q} = \Delta\beta/\alpha_0 \quad (6)$$

From equation 5,  $\ln M = (1-q) \ln \beta/\alpha_0$ . Since this is valid only when  $M$  is nearly one

$$1 - M = (1-q) \ln \alpha_0/\beta \quad (7)$$

Here,  $1 - M$  is the sum of the mole fractions of the dimethylpentanes. The data of run 2, Table II, fit this equation with a value of  $q$  of about 0.92. Thus, 8% of the methylhexane carbonium ions isomerize to dimethylpentane carbonium ions before step (c). This value is also consistent with run 1.

Equation 6 is tested against run 2 in the last column of Table V. Agreement is excellent. A similar test was made with mass spectroscopic data obtained from successive samples of emulsion collected in a run at 60° with 96.8% acid with stirring at least as good as rapid. Similar results were obtained. These runs show that, over a wide range of conversions, methylhexanes issue from step (c) in their equilibrium ratio but only a small fraction of this equilibrium mixture of ions isomerizes to ones of dimethylpentane structure before step (c).

Table I presents data permitting a test of the validity of equilibrium among the methylhexane carbonium ions over stirrings ranging from none to excellent. To simplify analysis, the small quantities of dimethylpentanes were ignored. If  $M = 1$  and  $q = 1$ , then from equation 6

$$X_2/X_2^{eq} = \Delta\beta/\alpha_0 \quad (8)$$

This relation is tested in Table V. Owing to neglect of dimethylpentanes the two terms do not agree as well as in the test of equation 6 but the computations show that results are independent of stirring and of presence or absence of oxygen.

TABLE V

COMPARISON OF ISOMERIZATION WITH LOSS IN ROTATION<sup>a</sup>

Run no.	$\Delta\beta/\alpha_0$	$X_2$	$X_2/X_2^{eq}$	$M$	$\frac{1 - (1 - X_2/X_2^{eq}M)^{1/n}}{X_2/X_2^{eq}M}$
Table I					
a	0.318	0.212	0.356		
b	.310	.224	.376		
c	.325	.232	.390		
d	.308	.207	.348		
e	.303	.191	.321		
f	.288	.191	.321		
g	.254	.188	.316		
j	.219	.142	.239		
m	.573	.317	.533		
n <sup>b</sup>	.388	.255	.429		

Table II

2, 30 min.	.167	.089	0.981	0.159
60 min.	.324	.177	.975	.328
120 min.	.594	.307	.936	.582
300 min.	.820	.410	.893	.801

<sup>a</sup>  $X_2$  is mole fraction of 2-methylhexane,  $M = X_2 + X_3$ ;  $\Delta\beta/\alpha_0$  is fractional loss in rotation. <sup>b</sup> This was a 3-hour run, otherwise like run c.

Initially, the relative rates of loss of rotation and isomerization stand roughly as 100:60. Our preliminary report on isomerization somewhat underestimated the relative degree of isomerization.<sup>2b</sup>

Ignoring the dimethylpentanes and starting with pure 3- or 2-methylhexane, then from equation 1

$$dX_3/dt = kX_3^{eq} \text{ (or } dX_2/dt = kX_3^{eq})$$

Whence, the ratio of the initial rates of isomerization of 3- and 2-methylhexane is  $X_2^{eq}/X_3^{eq}$  as observed for this system and also for 2,3- and 2,4-dimethylpentane,<sup>7</sup> in which case the ratio is  $x_{24}^{eq}/x_{23}^{eq}$ .

**Isotopic Exchange.**—In exchange between heavy sulfuric acid and alkane (Table IV), alkanes issuing from step (c) are assumed at isotopic equilibrium<sup>2</sup> although the hydrogen atom at the tertiary position will always be protium.<sup>4</sup> If the exchange equilibrium constant is unity

$$dD_h/dt = ((n - 1)/n)k(1 - D_h/D_h^{eq}) \quad (9)$$

and integrating for initially undeuterated hydrocarbon

$$-k = \frac{nD_h^{eq}}{(n - 1)t} \ln(1 - D_h/D_h^{eq}) \quad (10)$$

where  $n$  is the number of hydrogen atoms in the alkane<sup>9</sup> and  $D_h$  is the fraction of deuterium in the total hydrogen of the alkane.

As shown in Table V, runs c and d, the rates of exchange of 2- and 3-methylhexane are equal. These runs were made with the same batch of  $D_2SO_4$  under conditions as like as possible. Similar agreement obtains within other analogous sets: 2-, 3- and 4-methylheptane (i, h and f) and for 2,3- and 2,4-dimethylpentane (j and k). Only runs at the same ratios of hydrocarbon to acid should be compared, *i.e.*, at the same value of  $D_h^{eq}$ . The identity in rate is strong support for the proposed mechanism and in particular for identity within a set in rate of hydride ion transfer to sulfuric acid (step (a)) and of hydride ion transfer from members of a set.

(9) Equation 10 is derived in ref. 2a although now allowance is made for non-exchange of the tertiary position.<sup>4</sup> Here,  $D_h$  corresponds to  $X_{het}$  and  $D_h^{eq}$  to  $1/q$ .

From equations 4 and 10

$$(D_h^{eq}n/(n - 1)) \ln(1 - D_h/D_h^{eq}) = \ln(1 - \Delta\beta/\alpha_0) = -kt \quad (11)$$

For runs d, g and h of Table IV, the values of  $k$  computed from loss of rotation are 5.49, 2.81 and  $6.39 \times 10^{-5} \text{ sec.}^{-1}$ . These values slightly exceed those computed from deuterium exchange (Table IV) and in about the same degree as previously reported.<sup>2</sup> These values are derived from the same reaction product so that reproducibility in stirring is not a factor. Considering the assumption that the equilibrium constant for the exchange reaction is unity, agreement is good. The ratio of  $k$ 's from exchange and loss of rotation is independent of stirring (runs g and h). Thus, each molecule issuing from step (c) is substantially at equilibrium in regard to exchange.

The original mechanism plus the additional specific assumptions listed following the heading Mechanism agree with the absolute kinetics of racemization and isomerization, with the rate of appearance of dimethylpentanes, with the rates of exchange within sets of methyl shift isomers, and, in particular, the same rate constant serves, to a close approximation, for racemization, isomerization and exchange in the particular kinetic framework consequent to the mechanism. In particular, the assumption that carbonium ions come to equilibrium in regard to simple methyl shift before hydride ion transfer occurs is well supported.

Information on this last point is available from mass-spectroscopic investigation of isotopic exchange reactions.<sup>4b</sup> At 25°, the carbonium ion usually does not come to full equilibrium before hydride ion transfer. However, since the ratio of isomerization to hydride ion transfer increases with temperature,<sup>2b,4b,8</sup> it appears probable from the data of Stevenson, Wagner, Beeck and Otvos<sup>4b</sup> that at 60° isomerization equilibrium would very nearly be reached before hydride ion transfer. The requirements for such equilibrium are more stringent in isotopic exchange confined to hydrogen atoms contiguous to the tertiary position than in mere isomerization since, for example, 2- and 5-methylhexane are equivalent for isomerization but not for isotopic exchange. Isomerization of methylhexanes to dimethylpentanes is also relatively more rapid at 60° than at 25°.<sup>4b</sup>

**Methylheptanes.**—The lower precision of the analytical data in the much more complex case of the methylheptanes precludes a quantitative test of the model although, qualitatively, the model is satisfactory. The estimated proportion in an equilibrium mixture of 2-, 3- and 4-methylheptanes is 51:37:12.<sup>10</sup> The ratio in which the other two isomers appear when one of the methylheptanes is isomerized (Table III) agrees with this proportion qualitatively although the proportions, 42:36:22 would fit the data better and also the relative initial rates of isomerization. The difference is of doubtful significance in terms of either set of data.

The four dimethylhexanes should appear in their equilibrium order. From Table III and run 9

(10) P. D. Rossini in "Physical Chemistry of Hydrocarbons," edited by A. Farkas, Vol. I, Academic Press, Inc., New York, N. Y., 1950, p. 395.

(Experimental section) one can say that 2,4- and 2,5-dimethylhexane appear in roughly equal concentrations, 2,3-dimethylhexane in smaller quantity and 3,4-dimethylhexane in negligible quantity.

This is consistent with the best available estimate.<sup>10</sup> The relative rate of formation of the dimethylhexanes is faster than the corresponding rate of formation of dimethylpentanes.

**Chain Length.**—Sulfur dioxide should result from the chain initiation step. In vacuum line experiments, the condensable portion of the nitrogen atmosphere and the volatile portion of the reaction mixture was condensed into a side tube containing a known quantity of 0.3 *M* sodium hydroxide solution. The acidimetric determination of sulfur dioxide was followed by iodimetric determination of sulfite. The two methods agreed and demonstrated formation of sulfur dioxide. The rate constant for loss of rotation was 13 times greater than the rate of sulfur dioxide formation for 3-methylhexane and 11 for 3-methylheptane. These numbers represent minimum chain lengths. Since the products of chain ending are probably the cyclic, poly-olefinic hydrocarbons appearing in the sulfuric acid, considerable further oxidation is involved with formation of further sulfur dioxide. The true chain lengths are probably several times the listed figures.

These results were obtained with standard stirring. With the best stirring, good first-order kinetics were found to be beyond 60% loss of rotation unlike earlier procedures in which rate constants declined with time.<sup>11</sup> Water formation must accompany sulfur dioxide formation. Since the rate constants fall very rapidly with increasing water content,<sup>2a,4a,5</sup> the chain length appears longer with better stirring.

**Site of Reaction.**—The data cannot clearly decide whether the reaction occurs at the hydrocarbon-acid interface or in the acid phase. The solubility of *n*-octane in sulfuric acid was roughly measured by agitating it with acid and centrifuging the acid layer. The octane was removed from the acid layer by a stream of dry air and condensed in a Dry Ice trap. Its solubility is about 0.01 cc. per 100 cc. at 25°. About 1/4 this quantity of (+)3-methylheptane reacted per second in run 6, Table III.

**Disproportionation.**—Disproportionation was almost always observed in isomerization of methylheptanes and occasionally and to a much smaller extent with methylhexanes. Disproportionation is much more extensive with aluminum chloride. The disproportionation presumably proceeds *via* addition reactions to give large molecules or ions followed by cleavage.<sup>12</sup>

**Comparison of Sulfuric Acid and Aluminum Chloride in Isomerization and Racemization.**—The proposed mechanism for isomerization by sulfuric acid resembles that for aluminum chloride,<sup>13,14</sup> al-

though unlike aluminum halides sulfuric acid requires no added initiator and is unaffected by oxygen (Table I, runs a, b and c).

As proposed<sup>2</sup> only hydrocarbons containing tertiary hydrogen atoms are attacked by sulfuric acid. This has been confirmed.<sup>4b,5,15,16</sup> 3,3-Dimethylhexane is a new example of unreactive hydrocarbon (Table IV, run e). Likewise, only hydrocarbons containing at least one tertiary hydrogen atom have been identified as products of isomerization in this or other work.<sup>4b,5,6,15</sup> The non-formation of butane in treatment of isobutane with sulfuric acid<sup>4a</sup> and of cyclohexane in treatment of methylcyclopentane (run m, Table V) are particularly good examples of this.

Those isomerizations which seem not to occur in sulfuric acid occur more slowly with aluminum halides,<sup>17</sup> but hydrocarbons such as butane and cyclohexane are isomerized and formed by aluminum halides.

Thus, with aluminum halides, hydride ion transfer occurs to and from secondary positions but not to or from primary positions since *neopentane* is not formed in isomerization of pentanes; whereas with sulfuric acid hydride ion transfer is limited to and from tertiary positions.

Application of the mechanism for isomerization of carbonium ions<sup>13,14</sup> involves formation of primary carbonium ions during the isomerization step. As applied to sulfuric acid, secondary carbonium ions would be required. Such ions should be more active in abstracting hydride ions than tertiary carbonium ions would be. Yet such abstraction seems to occur at negligible rate. It seems better not to assume that species with the *general* behavior of secondary and primary carbonium ions are present in isomerization with sulfuric acid or primary carbonium ions with aluminum halides.

At 23°, (+)3-methylhexane is racemized by aluminum chloride and isomerized to 2-methylhexane.<sup>18</sup> The chain carrying carbonium ion does not come to equilibrium in regard to methyl shift before hydride ion transfer occurs. This is also true of sulfuric acid at these temperatures,<sup>4b,8</sup> although probably the approach to equilibrium is closer with sulfuric acid.

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(11) See also ref. 5.

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