trum differs from that of (III) by the absence of bands at 830 and 699 cm.$^{-1}$, and the presence of strong bands at 911, 1215, 1674 and 1741 cm.$^{-1}$ ($COCH_2OCOCH_3$).[16]

Anal. Calcd. for $C_{22}H_{26}O_6S_2$: C, 58.64; H, 5.82. Found: C, 58.31; H, 6.00.

This investigation was supported by grants from the American Cancer Society, as recommended by the Committee on Growth of the National Research Council, and the Jane Coffin Childs Memorial Fund for Medical Research.

CHICAGO 37, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, STANDARD OIL CO. (INDIANA)]

Sulfuric Acid Isomerization of Methylalkanes, Dimethylalkanes and Dimethylcyclohexanes

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RECEIVED OCTOBER 27, 1952

Sulfuric acid was investigated as a catalyst for the isomerization of fourteen alkanes and cycloalkanes, and the rate of approach to equilibrium was measured. Increasing the initial acid concentration from 95.5 to 99.8% increased the rate of isomerization as much as 64-fold. Equilibrium compositions determined experimentally agree well with those calculated from heats of combustion, except for the interconversion of 2,3-dimethylpentane and 2,4-dimethylpentane. No significant change in the degree of branching of the hydrocarbon chain was observed, but methyl groups migrated readily. Rearrangements occur only at a tertiary carbon and are of three kinds: a rapid rearrangement of methyl groups with respect to plane, as in geometric isomers; a less-rapid shift of a methyl group along the hydrocarbon chain; and a relatively slow shift of a methyl group around the hydrocarbon ring.

Introduction

Considerable work has been done on the isomerization of various alkanes and naphthenes with sulfuric acid as the catalyst, but little has been reported on isomerization rates. The sulfuric acid isomerization of alkanes has been studied largely in connection with the products that result from alkylation.[1] Gordon and Burwell[2] compared the isomerization rates of several methylalkanes, and showed that sulfuric acid racemizes optically active 3-methylheptane; normal paraffins and those containing quaternary carbons are not isomerized. Certain methylalkanes and dimethylalkanes have been isomerized with little side reaction; the conversions were limited by equilibria.[3] Measurement of the relative rates of isomerization of the isomeric hexanes with aluminum chloride showed the interconversion of 2- and 3-methylpentane to be the most rapid reaction.[4]

No work has been reported on the sulfuric acid isomerization of the dimethylcyclohexanes, although a study with dimethylcyclopentane has recently been reported.[5] Isomerization of dimethylcyclohexanes with aluminum chloride gives largely *cis*-1,3-dimethylcyclohexane, the most stable isomer.[6] The *cis–trans* isomerization of the 1,2- and 1,4-dimethylcyclohexanes was observed by Zelinsky and Margolis,[7] who passed the hydrocarbons over active nickel at 175°. With aluminum chloride,[8] *cis*-1,2-dimethylcyclopentane was converted rapidly to the *cis–trans* equilibrium mixture, which was then converted slowly to methylcyclohexane.

The present paper deals with the quantitative measurement of equilibria and with the effects of sulfuric acid concentration and hydrocarbon structure on the isomerization rates of fourteen hydrocarbons. Sulfuric acid gives rise to a minimum of side reactions and thus permits more accurate measurement of equilibria and isomerization rates.

Experimental

2-Methylpentane, 3-methylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane and 2,3-dimethylhexane were obtained from the Phillips Petroleum Co. and used without further purification. Grignard synthesis followed by dehydration of the alcohol and hydrogenation of the olefin was used to prepare 2-methylhexane, 3-methylhexane and 2,4-dimethylhexane. 3-Methylheptane was prepared from 2-ethylhexanol by dehydration and hydrogenation. The synthesized alkanes were fractionated in a 1-inch Stedman column of 60 theoretical plates, and fractions having the accepted boiling points and refractive indices were retained. Dimethylcyclohexanes were prepared by hydrogenating the individual xylenes and separating the *cis* and *trans* isomers in the Stedman column. In the case of *m*-xylene, which was contaminated with *p*-xylene, only *cis*-1,3-dimethylcyclohexane could be isolated. Physical constants of all fourteen hydrocarbons are compared with the values of Rossini[9] in Table I; the indicated purities were determined by mass-spectrometric analysis of the alkanes and by infrared analysis of the dimethylcyclohexanes. The hydrocarbons were free of olefins, as determined by negative reaction with potassium permanganate, and contained less than 3 p.p.m. of peroxide.[10]

Sulfuric acid of the desired concentration was prepared by mixing commercial 96% acid and fuming sulfuric acid. The actual strength was established with an accuracy of ±0.1% by titration against 0.2 *N* sodium hydroxide.

The isomerization studies were made by vigorously stirring the hydrocarbon with an equal weight of sulfuric acid in a round-bottomed flask equipped with a wire-loop stirrer[11]

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(1) P. D. Caesar and A. W. Francis, *Ind. Eng. Chem.*, **33**, 1426 (1941); S. F. Birch and A. F. Dunstan, *Trans. Faraday Soc.*, **35**, 1013 (1939); F. Morton and A. R. Richards, *J. Inst. Petroleum*, **34**, 133 (1948).

(2) G. Gordon and R. L. Burwell, THIS JOURNAL, **71**, 2355 (1949).

(3) V. I. Komarewsky and W. E. Reuther, *ibid.*, **72**, 5501 (1950).

(4) B. L. Evering and R. C. Waugh, *Ind. Eng. Chem.*, **43**, 1820 (1951).

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

(6) G. Egloff, G. Hulla and V. I. Komarewsky, "Isomerization of Pure Hydrocarbons," Reinhold Publ. Corp., New York, N. Y., 1942; G. Chiurdoglu, P. J. C. Fierens and C. Henkart, *Bull. soc. chim. Belg.*, **59**, 140 (1950).

(7) N. D. Zelinsky and E. I. Margolis, *Ber.*, **65B**, 1613 (1932).

(8) G Chiurdoglu, *Bull. soc. chim. Belg.*, **53**, 55 (1944).

(9) F. D. Rossini, "Selected Values of Properties of Hydrocarbons," U. S. Govt. Printing Office, Washington, 1947.

(10) The possible effect of such trace impurities as peroxides and olefins was considered. The addition of gross amounts of *t*-butyl peroxide (600 p.p.m.) and potassium persulfate (400 p.p.m.) about doubled the isomerization rate. Addition of 0.1% 2-methylbutene-2 or cyclohexene decreased the isomerization rate slightly.

(11) E. B. Hershberg, *Ind. Eng. Chem.*, *Anal. Ed.*, **8**, 313 (1936).

TABLE I

PHYSICAL CONSTANTS AND PURITY OF HYDROCARBONS

Hydrocarbon	Observed		Literature[a]		Purity, mol. %	Impurity
	B.p., °C.[b]	$n^{20}\text{D}$	B.p., °C.	$n^{20}\text{D}$		
2-Methylpentane	60.3	1.3715	60.27	1.3714	97.1	1.4% 3-Methylpentane 1.5% 2,3-Dimethylbutane
3-Methylpentane	63.2	1.3765	63.28	1.3765	99.5	0.5% 2-Methylpentane
2,3-Dimethylpentane	89.7	1.3919	89.79	1.3920	94.8	1.6% 3-Methylhexane 3.6% 2-Methylhexane
2,4-Dimethylpentane	80.3	1.3815	80.51	1.3816	99.2	0.8% 2-Methylhexane
2-Methylhexane	90.0	1.3848	90.05	1.3849	98.3	1.7% 3-Methylhexane
3-Methylhexane	91.9	1.3885	91.95	1.3887	99.5	0.5% 2,3-Dimethylpentane
2,3-Dimethylhexane	115.6	1.4015	115.6	1.4015	92.2	2.4% 2,5-Dimethylhexane 1.4% 2,4-Dimethylhexane 3.0% 3-Methylheptane 0.6% 2-Methylheptane 0.4% 4-Methylheptane
2,4-Dimethylhexane	109.1	1.3953	109.4	1.3953	[c]	......
3-Methylheptane	118.8	1.3985	118.9	1.3985	98.4	0.3% 2-Methylheptane 0.7% 2,3-Dimethylhexane 0.6% 2,4-Dimethylhexane
cis-1,2-Dimethylcyclohexane	129.0	1.4361	129.7	1.4360	99	0.2% *trans*-1,4-
trans-1,2-Dimethylcyclohexane	123.0	1.4271	123.4	1.4270	99	(None detected)
cis-1,3-Dimethylcyclohexane	119.0	1.4229	120.1	1.4229	96	1.0% *trans*-1,4- 3.0% *cis*-1,2- and *trans*-1,3-
cis-1,4-Dimethylcyclohexane	119.0	1.4209	120.1	1.4209	99	0.5% *cis*-1,2- 0.5% *trans*-1,3-
trans-1,4-Dimethylcyclohexane	124	1.4295	124.3	1.4297	98	1–2% *cis*-1,3-

[a] See ref. 9. [b] Not corrected for barometric pressure. [c] Not determined.

and a mercury seal. Reaction temperature was maintained by immersing the flask in a bath at 25° unless otherwise specified. The mixture gave the appearance of an emulsion but readily separated into two well-defined layers within two minutes after stopping agitation. At predetermined intervals, agitation was interrupted and samples of the acid and hydrocarbon layers were taken. The hydrocarbon samples were analyzed by refractive index, fractionation, mass spectrometer and infrared spectrometer.

The isomerization rate was determined by calculating the reaction velocity constant from the equation for a reversible first-order reaction

$$k = \frac{X_e}{at} 2.3 \log \frac{X_e}{X_e - X}$$

where X_e is the equilibrium quantity of the component being formed, a is the quantity of starting material, t is the reaction time in hours, and X is the quantity of isomerization product at time t. The values for k, computed from zero time, decline during a run because of a decrease in catalyst activity, as shown in the following table for 3-methylpentane.

t, hours	0.25	0.5	1	2	3	4
k, hr.$^{-1}$	.61	.58	0.50	0.39	0.34	0.30

To minimize this effect the isomerization rates of the various hydrocarbons were recorded at the uniform time of one hour. Rate measurements for all the hydrocarbons were based on at least three determinations. Where no evidence of isomerization was detected, the reaction rate was less than 0.0002.

Results

Acid Concentration.—The initial strength of the sulfuric acid had a marked effect on isomerization rate. As shown in Fig. 1 for 3-methylpentane, the isomerization rate increased rapidly as the acid strength was increased and reached a sharp peak at 99.8%, after which it declined sharply. This optimum in acid concentration appears to be independent of hydrocarbon structure, as a sharp peak at 99.8% was likewise found for 2,3-dimethylpentane and 2,4-dimethylpentane and for *cis*- and *trans*-1,4-dimethylcyclohexane.

The change in acid strength during isomerization was determined for acids of various initial concentrations. Higher initial concentrations gave faster and greater declines in acid strength, as shown in Fig. 2 for 3-methylpentane. The rapid decline during the first hour later leveled off to a slow and constant decline.

Equilibrium Compositions.—The equilibrium compositions were approached from both sides by isomerizing each hydrocarbon separately at 25° with 99.8% sulfuric acid. Dimethylpentanes required the addition of 12% fluosulfonic acid[12] because of their slow isomerization rate. The mixed acid about doubles the isomerization rate. The compositions of the mixtures for 2-methylpentane and 3-methylpentane, for 2,3-dimethylpentane and 2,4-dimethylpentane, and for 2-methylhexane and 3-methylhexane are plotted against time in Figs. 3, 4 and 5. The percentages of the hydrocarbon pairs are adjusted to a 100% basis by excluding the small quantities of other isomers formed; actual concentrations of the minor isomers are shown at the bottom of each plot. In the methylpentane system, a small quantity of 2,3-dimethylbutane was formed; no *n*-hexane or 2,2-dimethylbutane was observed. With the dimethylpentanes, there was a slow formation of

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(12) A. K. Roebuck and B. L. Evering, U. S. Patent 2,564,080 (August 14, 1951).

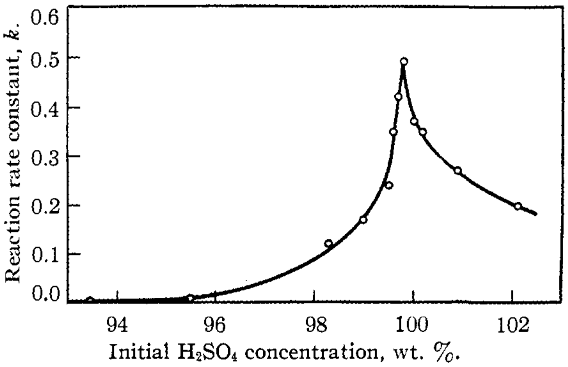

Fig. 1.—Effect of acid strength on reaction rate of 3-methylpentane.

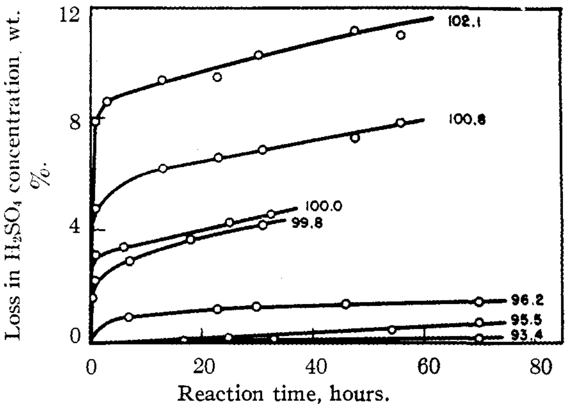

Fig. 2.—Decline in sulfuric acid concentration with time.

2-methylhexane and 3-methylhexane; mass spectrometric analysis gave no evidence of other heptane isomers. In establishing equilibrium between the methylhexanes, the formation of a small amount of 2,4-dimethylpentane and 2,3-dimethylpentane was detected.

The equilibrium compositions determined for the methylalkanes, summarized in Table II, show reasonable agreement with the literature values obtained at 20° with aluminum chloride as the catalyst. With one exception, they also agree with the thermochemical values calculated from heats of combustion; the calculated equilibrium composition for 2,3-dimethylpentane and 2,4-dimethylpentane is in complete disagreement with the experimental determinations.

TABLE II

EQUILIBRIUM COMPOSITION OF ALKANES IN LIQUID PHASE AT 25°

Hydrocarbon	Equilibrium composition, mole % Refractive index[a]	Spectrograph	Literature[b]	Thermochemical[c]
2-Methylpentane	68	69	72	71
3-Methylpentane	32	31	28	29
2,3-Dimethylpentane	35	34	40	79
2,4-Dimethylpentane	65	66	60	21
2-Methylhexane	56	59	62	52
3-Methylhexane	44	41	38	48

[a] Limit of error ±2%. [b] Values at 20° from J. J. B. Von Eijk Von Voorthuijsen, *Rec. trav. chim.*, **66**, 323 (1947). [c] Values for vapor phase from Rossini[9] converted to liquid phase by using vapor pressure of hydrocarbons from *b* and assuming ideal mixtures.

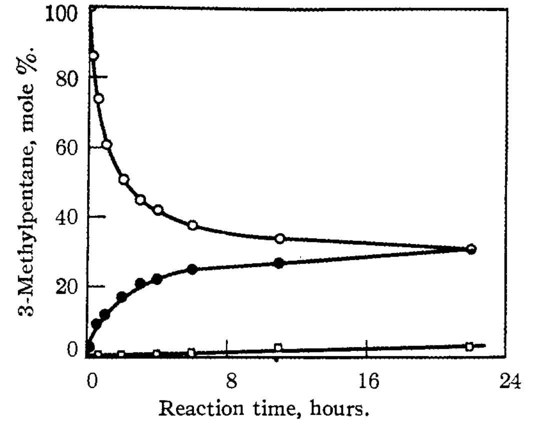

Fig. 3.—Equilibrium composition of 2-methylpentane and 3-methylpentane at 25°: starting with: ⊙, 3-methylpentane; ●, 2-methylpentane; also formed: □, 2,3-dimethyl butane.

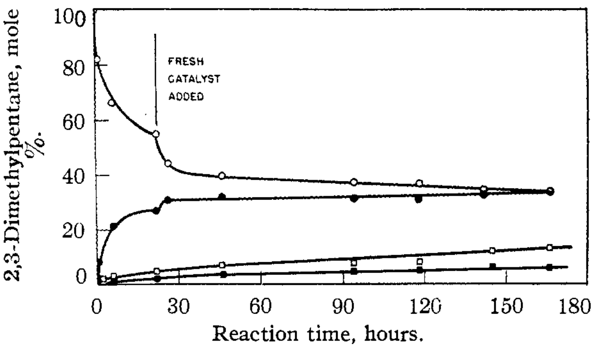

Fig. 4.—Equilibrium composition of 2,3-dimethylpentane and 2,4-dimethylpentane at 25°: starting with: ⊙, 2,3-dimethylpentane; ●, 2,4-dimethylpentane; also formed □, 2-methylhexane; ■, 3-methylhexane.

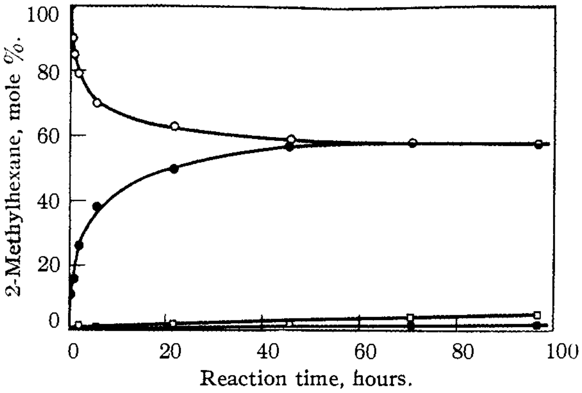

Fig. 5.—Equilibrium composition of 2-methylhexane and 3-methylhexane at 25°: starting with: ⊙, 2-methylhexane; ●, 3-methylhexane; also formed: □, 2,4-dimethylpentane; ■, 2,3-dimethylpentane.

The equilibria between the *cis* and *trans* isomers of the dimethylcyclohexanes were investigated with 99.8% acid and plotted in the manner used for the alkanes. The composition of the mixtures of *cis* and *trans* isomers for 1,4-dimethylcyclohexane, 1,2-dimethylcyclohexane and 1,3-dimethylcyclohexane are plotted against time in Figs. 6, 7 and 8. Only in the case of 1,4-dimethylcyclohexanes was equilibrium established by starting with

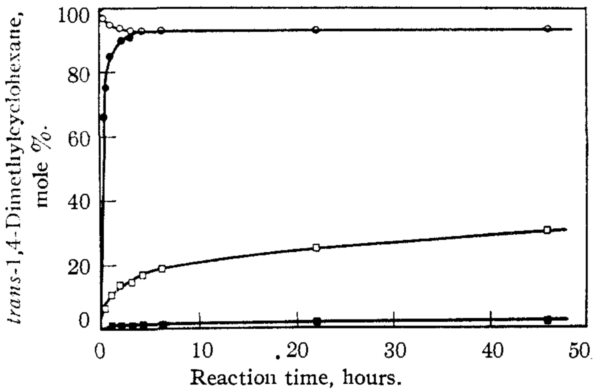

Fig. 6.—Equilibrium composition of *cis*- and *trans*-1,4-dimethylcyclohexane at 25°: starting with: ⊙, *trans*-1,4-dimethylcyclohexane; ●, *cis*-1,4-dimethylcyclohexane; also formed: □, *cis*-1,3-dimethylcyclohexane; ■, *trans*-1,3-dimethylcyclohexane.

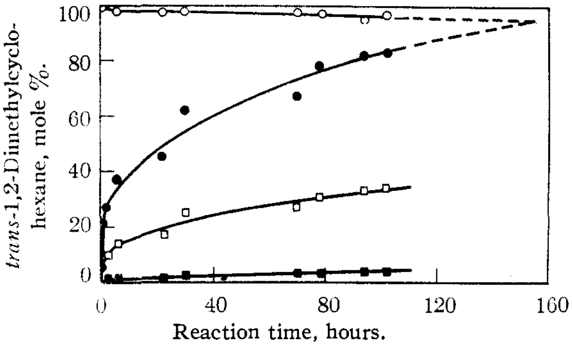

Fig. 7.—Equilibrium composition of *cis*- and *trans*-1,2-dimethylcyclohexane at 25°: starting with: ⊙, *trans*-1,2-dimethylcyclohexane; ●, *cis*-1,2-dimethylcyclohexane; also formed: □, *cis*-1,3-dimethylcyclohexane; ■, *trans*-1,3-dimethylcyclohexane.

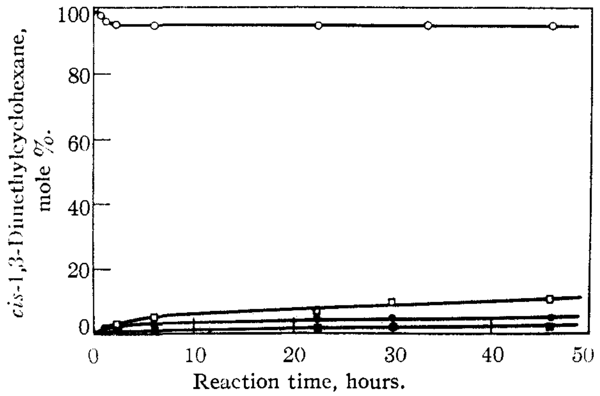

Fig. 8.—Equilibrium composition of *cis*- and *trans*-1,3-dimethylcyclohexane at 25° starting with *cis*-isomer only: ⊙, *cis*-1,3-dimethylcyclohexane; ●, *trans*-1,3-dimethylcyclohexane; also formed: □, *trans*-1,4-dimethylcyclohexane; ■, *trans*-1,2-dimethylcyclohexane.

both isomers. Besides the interconversion of *cis* and *trans* isomers, there was considerable isomerization to *cis*-1,3-dimethylcyclohexane, the thermodynamically predominant isomer among the C_8-naphthenes. Although the *cis* and *trans* isomers of 1,2-dimethylcyclohexane were contacted with 99.8% acid for 106 hours, equilibrium was not established. However, a reasonable extrapolation to equilibrium is shown by the dashed portion of the curves. The principal methyl shift was again formation of the 1,3-dimethylcyclohexanes. The *cis–trans* equilibrium for 1,3-dimethylcyclohexane could only be established from one side because only the *cis* isomer was available. The rapid conversion of the *cis* to the *trans* isomer that occurred during the first two hours, with little or no change thereafter, indicated that equilibrium was established. No detectable quantities of trimethylcyclopentanes were found from any of the dimethylcyclohexanes. Excellent agreement exists between the experimentally determined equilibria for the *cis* and *trans* isomers of the dimethylcyclohexanes and the values determined from thermochemical data, as shown in Table III.

Table III

Equilibrium Composition of Dimethylcyclohexanes in Liquid Phase at 25°

Hydrocarbon	Equilibrium composition, mole % Observed	Thermochemical[a]
cis-1,4-Dimethylcyclohexane	7	10
trans-1,4-Dimethylcyclohexane	93	90
cis-1,3-Dimethylcyclohexane	95[b]	94
trans-1,3-Dimethylcyclohexane	5[b]	6
cis-1,2-Dimethylcyclohexane	5[c]	7
trans-1,2-Dimethylcyclohexane	95[c]	93

[a] Values from Rossini[9] converted to liquid phase by using vapor pressure of hydrocarbons given by Willingham, *et al.*, *J. Research Natl. Bur. Standards*, **35**, 219 (1945), and assuming ideal mixtures. [b] Equilibrium approached from *cis*-1,3-dimethylcyclohexane side only. [c] Equilibrium estimated by extrapolation.

Isomerization Rates.—The isomerization rates for the hydrocarbons with 99.8% acid were calculated from the equilibrium curves at one hour reaction time. Rate measurements were also obtained on 2,3-dimethylhexane, 2,4-dimethylhexane, 3-methylheptane and 2-methylheptane by using the values of Rossini for equilibrium.[9] The resulting isomerization rates are given in Table IV for the alkanes and in Table V for the dimethylcyclohexanes. On contact with acid for periods as long as

Table IV

Isomerization Rates of Methylalkanes

At 25° with 99.8% sulfuric acid for 1.0 hour

Isomerization reaction	*k*, hr.$^{-1}$	Accuracy[a]
2-Methylpentane → 3-methylpentane	0.14	±0.02
3-Methylpentane → 2-methylpentane	.49	.03
2-Methylhexane → 3-methylhexane	.18	.03
3-Methylhexane → 2-methylhexane	.17	.03
2,3-Dimethylpentane → 2,4-dimethylpentane	.15	.01
2,4-Dimethylpentane → 2,3-dimethylpentane	.05	.01
3-Methylheptane → 2-methylheptane	.18	[b]
2,4-Dimethylhexane → 2,5-dimethylhexane	.54	[b]

[a] Limits of error of *k* based on accuracy of hydrocarbon analysis. [b] Accuracy of hydrocarbon analysis unknown.

Table V

Isomerization Rates of Dimethylcyclohexanes

At 25° with 99.8% sulfuric acid for 1.0 hour

Isomerization reaction	k, hr.$^{-1}$
cis-1,4- → *trans*-1,4-	1.5
trans-1,4- → *cis*-1,4-	0.08
cis-1,4- → *cis*-1,3-	.12
trans-1,4- → *cis*-1,3-	.09
cis-1,2- → *trans*-1,2-	.22
trans-1,2- → *cis*-1,2-	.0002
cis-1,2- → *cis*-1,3-	.09
trans-1,2- → *cis*-1,3-	.02
cis-1,3- → *trans*-1,3-	.06
cis-1,3- → *trans*-1,2-	.009
cis-1,3- → *trans*-1,4-	.04

150 hours, *n*-hexane, 2,3-dimethylbutane, methylcyclopentane and cyclohexane gave no evidence of isomerization detectable by refractive index.

The rates of isomerization of 3-methylpentane and 2,3-dimethylpentane vary little with changes in temperature. Measurement of the rates over the range of 10–50° gave straight lines when log k was plotted against $1/T$, as shown in Fig. 9. The slopes of these lines give an activation energy of 6,400 cal. per mole for 3-methylpentane and of 4,900 cal. per mole for 2,3-dimethylpentane. Temperatures above 50° could not be investigated because of oxidation of the hydrocarbons.

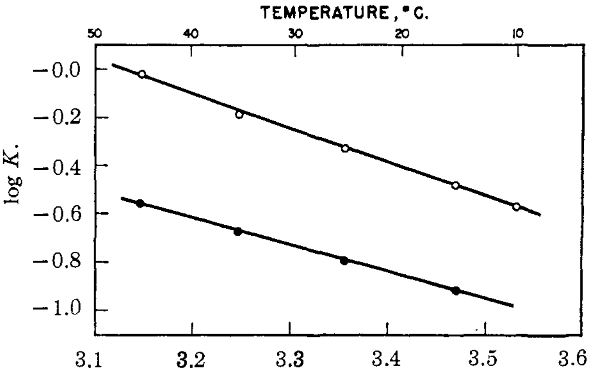

Fig. 9.—Effect of temperature on reaction rate: ○, 3-methylpentane; ●, 2,3-dimethylpentane.

Discussion

Isomerization rates are strongly influenced by the initial sulfuric acid concentration, maximum activity occurring at 99.8%. Above this concentration, isomerization activity declines because of rapid dilution of the acid by the degraded hydrocarbons; this decline more than offsets any increased activity of the higher-strength acids. The 64-fold increase in isomerization rate between 95.5 and 99.8% sulfuric acid is strikingly similar to the rapid increase in acid function (H_0) as measured by Hammett for sulfuric acid.[13] Otvos and co-workers[14] have reported that the rate of exchange of isobutane-1-*d* with sulfuric acid is proportional to the acid function over the range of 91.5 to 98.3% sulfuric acid. The isomerization rate for 3-methylpentane thus parallels the rate of hydrogen exchange. These similarities suggest some interdependence between isomerization and hydrogen exchange, in keeping with the findings of Stevenson and co-workers.[5]

Hydrocarbon structure has a pronounced effect on isomerization rate. Hydrocarbons containing only primary and secondary carbon atoms do not isomerize, as exemplified by the behavior of *n*-hexane and cyclohexane. The only isomerizations observed take place with hydrocarbons containing tertiary carbon atoms, and even then certain rearrangements do not occur. Methylcyclopentane shows no evidence of ring enlargement; methylalkanes and dimethylalkanes show only minor indications of change in the degree of branching. The only rearrangements occurring at measurable rates with sulfuric acid are the shift of methyl groups (a) about the plane in geometric isomers, (b) along the hydrocarbon chain, and (c) around the ring in the dimethylcyclohexanes. Although complications arising from steric hindrance, position of equilibrium, and perhaps other factors cause considerable overlapping in the rates of these rearrangements, it appears that the most rapid shift involves rearrangement of a methyl group about a single carbon atom, the next most rapid is the shift of a methyl group along the hydrocarbon chain, and the slowest is the shift of a methyl group around the hydrocarbon ring of a dimethylcyclohexane.

Acknowledgment.—The authors are indebted to Seymour Meyerson for the mass spectrometric analyses and to R. R. Hopkins for the infrared analyses.

Whiting, Indiana

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[13] L. P. Hammett, *Chem. Revs.*, **16**, 67 (1935).

[14] J. W. Otvos, D. P. Stevenson, C. D. Wagner and O. Beeck, *J. Chem. Phys.*, **17**, 418 (1949).