Isomerization Equilibrium among the Branched Chain Pentenes[1]

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The entropies of hydrocarbon vapors are useful for the theoretical calculation of equilibrium constants involving hydrocarbons. Entropies can be obtained from (1) calculation using the methods of statistical mechanics, (2) heat capacity data utilizing the third law of thermodynamics, and (3) equilibrium measurements. The last method is used in this work to determine the entropy differences between the isomeric branched chain pentenes. If equilibrium can be established among the isomers and the product analyzed, the several equilibrium constants can be determined. Combining these equilibrium constants with the heats of isomerization, which can be calculated from the heats of hydrogenation reported by Kistiakowsky and co-workers,[3] the entropy change or entropy difference between any two isomers can be computed. Whenever an absolute entropy determination becomes available on one of the isomers, it will be possible to calculate the absolute entropies of the rest of the isomers.
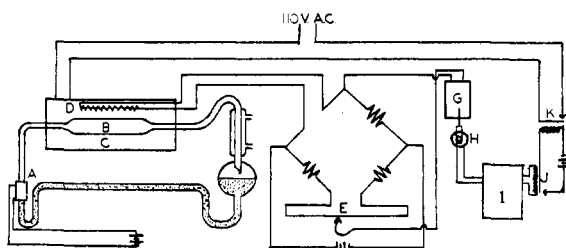

Fig. 1.—Isomerization apparatus and Wheatstone bridge photoelectric regulator for electric furnace.

The boiling points and densities (20°) of the pentenes are

	B. p., °C.	d^{20}
3-Methyl-1-butene	20.1	0.6340
1-Pentene	30.1	.6429
2-Methyl-1-butene	31.0	.6504
trans-2-Pentene	35.8	.6482
cis-2-Pentene	37.0	.6503
2-Methyl-2-butene	38.6	.6596

On distilling a mixture containing all six isomers,

three principal fractions would be expected: (1) 3-methyl-1-butene, (2) 1-pentene and 2-methyl-1-butene, and (3) cis- and trans-2-pentene and 2-methyl-2-butene.

It was found that with the catalysts used and at the temperatures at which the experiments were carried out, there was no evidence of chain branching or unbranching, which is in agreement with the findings of Norris and Reuter.[4] Other catalysts or higher temperatures are evidently required to promote branching and unbranching as well as double bond shift. Therefore this work devolved principally into a study of the equilibrium among the branched chain pentenes. Equilibrium among the straight chain pentenes cannot be studied with much accuracy since an exceedingly efficient fractionating column would be required to separate the cis- and trans-2-pentenes.

Experimental

Various pure pentene isomers were isomerized in the vapor phase by pumping them over solid catalysts in a sealed apparatus held at desired temperatures. The resulting mixtures were then analyzed by distilling in an efficient fractionating column. The experiments were made using batches of about 165 ml. of liquid. Because of the volatility of the pentenes, all handling and transferring operations were done after cooling with dry-ice, and the fractionating columns were equipped with dry-ice return traps. In spite of these precautions the over-all loss for all operations was 5 to 10 ml.

The Isomerization Apparatus.—The isomerization experiments were carried out in a sealed glass apparatus, shown in Fig. 1. The liquid was pumped by a vapor pump (A) over the catalyst (B) in the electric furnace (C) for a given length of time. The vapors leaving the catalyst were condensed and returned to the vapor pump thereby being continuously recirculated. The diameter of the tube at (A) was small enough that there was complete vaporization of the liquid, i. e., no selective distillation. The pressures in the apparatus were slightly above atmospheric due to the high temperatures used, but excessive pressures were not encountered unless cracking took place.

The number of times the entire sample passed over the catalyst was determined by counting the drops from the condenser. Each experiment was run at a rate of about two drops of liquid per second, which corresponds to 10 passes per twelve hours. Since all the experiments were run at approximately this same speed, it is not included in the tables, but the length of time each experiment was permitted to run is given.

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(3) Kistiakowsky, Ruhoff, Smith and Vaughan, THIS JOURNAL, 58, 137 (1936); Dolliver, Gresham, Kistiakowsky and Vaughan, ibid., 59, 831 (1937).

(4) Norris and Reuter, ibid., 49, 2624 (1927).

The temperature of the furnace was measured during each experiment by means of a thermocouple placed beside the catalyst tube in the furnace. The actual temperature of the catalyst mass itself was measured in several experiments with the aid of three thermocouples embedded in the catalyst tube. It was found that when the furnace temperature was 375°, the catalyst temperature was 20° lower, and when the furnace temperature was 325°, the catalyst temperature was 15° lower. In the rest of the experiments only the furnace temperatures were measured, and these were corrected to actual catalyst temperatures on the basis of the above data. For purposes of simplification all temperatures given in the rest of this paper will be catalyst temperatures, i. e., the measured furnace temperatures minus the appropriate corrections.

The temperature of the furnace was controlled by a regulator utilizing a Wheatstone bridge arrangement and a photoelectric control mechanism, shown in Fig. 1. The resistance coil (D), located adjacent to the catalyst tube in the furnace, is made of pure nickel wire and is one arm of the Wheatstone bridge. The other arms of the bridge are of manganin wire at room temperature. At any desired temperature the bridge is balanced by sliding the contact (E) along a short piece of manganin wire. When the temperature changes the bridge becomes unbalanced and the needle of the galvanometer (G) swings away from its zero point. A thin vane of aluminum attached to the galvanometer needle uncovers a small opening above a photoelectric cell (H), allowing light to strike the cell. The photocell current is amplified by a photocell relay (I), and the amplified current operates a sensitive relay (J), which opens a power relay (K), which controls the current to the furnace. The furnace current is thus shut off until the temperature decreases, bringing the bridge into balance again. This shuts the light from the photocell, closing the power relay and allowing the furnace to heat again. This regulator proved very dependable, holding the furnace temperature within a few degrees anywhere in the range of 250–400° for a day at a time

The Fractionation Apparatus.—Two fractionating columns were constructed, each containing 65 inches of one-half inch spiral screen packing,[5] which tested 80 theoretical plates at total reflux. The holdup of each column was about 15 ml. This large a holdup necessitated using a fairly large sample (165 ml.) so that each fraction could be determined accurately on the distillation curve. Since a high reflux ratio was required, each fractionation took a number of days. Therefore, the columns were made automatic so they could be run day and night without attention.

A column head was designed with an electrically operated, intermittent take-off mechanism, shown in Fig. 2. The column is operated at total reflux (mercury level at A) until liquid–vapor equilibrium is reached, at which time the solenoid (B) is actuated by an electric time switch

Fig. 2.—Electrically operated intermittent take-off head for fractionating column.
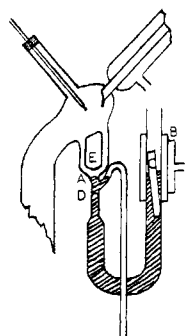
that can be set for any time cycle. The iron plunger (C), which is floating on the mercury, is pulled up into the solenoid, thereby dropping the mercury level to (D) and allowing the contents of the U-tube (E), about 2 ml., to siphon over into the receiver. After five seconds the time switch breaks the circuit, the plunger drops back into the mercury, and the column again runs at total reflux.

The length of time required to reach equilibrium after each 2-ml. take-off varied from five to sixty minutes depending on the portion of the distillation curve concerned. One take-off per hour was the usual operating rate since this would cover all requirements. The boiling rate was about 160 ml. of liquid per hour, so that the rate of take-off was equivalent to a reflux ratio of 80–1. Sometimes on a long plateau the rate of take-off was increased to 2, 4, 6 or 12 times (2 ml. each) per hour, which correspond to reflux ratios of 40, 20, 13.3 and 6.6, respectively.

The temperature at the column head was measured by a six-junction copper–constantan thermocouple, the e. m. f. of which was continuously recorded on a recording potentiometer. This rendered the distillation entirely automatic, the distillation curve being obtained directly from the recorder chart.

The volumes of the fractions were determined in the usual way by measuring from the midpoints of the intermediate cuts. The accuracy of the analyses based on volume distilled was about ±0.5%. Duplicate experiments, 43 and 48, 45 and 47, 41 and 49, and 44 and 46, shown in Tables I and III, were found to agree within these limits.

Figure 3 shows the distillation curve obtained from the fractionation of a synthetic mixture containing all the pentene isomers. The curve shows that with the column used it was impossible to separate 1-pentene and 2-methyl-1-butene (boiling point difference 0.9°). Nevertheless there was a gradual increase in boiling point over the range in which these two isomers distilled. It was found possible, however, to make a fair separation of 2-pentene from 2-methyl-2-butene (boiling point difference 1.6° to 2.8°). The fractionation analysis of the synthetic mixture agreed with the known composition within 0.5%, when 1-pentene and 2-methyl-1-butene were combined as one fraction.
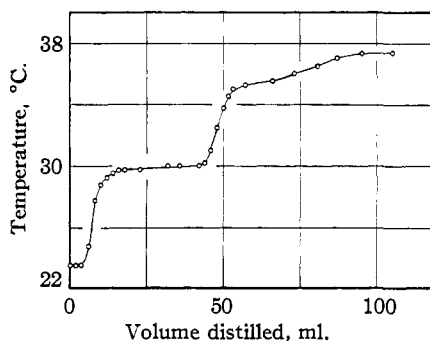

Fig. 3.—Distillation curve of a synthetic mixture containing all the isomeric pentenes.

A typical distillation curve of a mixture obtained from the isomerization of 2-methyl-2-butene is given in Fig. 4. The middle and upper plateaus are seen to be perfectly flat and show no indications of more than one component. Be-

(5) Lecky and Ewell, Ind. Eng. Chem., Anal. Ed., 12, 544 (1940).

TABLE I
ISOMERIZATION OF BRANCHED CHAIN PENTENES

Expt.	Catalyst	Starting material	Temp., °C.	Time, hr.	3-Methyl-1-butene	2-Methyl-1-butene	2-Methyl-2-butene
65	Act. alumina	2-Methyl-2-butene	263	3	0	17.5	82.5
66	Act. alumina	2-Methyl-2-butene	266	12	0.6	22.4	77.0
74	Act. alumina	2-Methyl-2-butene	251	24	1.9	22.8	75.3
34	Al$_2$O$_3$–CoO	2-Methyl-2-butene	311	12	1.2	11.3	87.5
43	Al$_2$O$_3$–MnO	2-Methyl-2-butene	310	12	1.3	21.3	77.4
48	Al$_2$O$_3$–MnO	2-Methyl-2-butene	300	12	1.9	21.3	76.8
27	Al$_2$O$_3$–Cr$_2$O$_3$	2-Methyl-2-butene	294	12	2.6	25.3	72.1
23	Al$_2$O$_3$–Fe$_2$O$_3$	2-Methyl-2-butene	296	12	1.3	26.5	72.2
63	Act. alumina	2-Methyl-2-butene	300	3	0.6	20.2	79.2
50	Act. alumina	2-Methyl-2-butene	300	12	2.6	25.8	71.6
32	Al$_2$O$_3$–CoO	2-Methyl-2-butene	370	12	6.3	26.0	67.7
45	Al$_2$O$_3$–MnO	2-Methyl-2-butene	361	12	4.3	26.1	69.6
47	Al$_2$O$_3$–MnO	2-Methyl-2-butene	363	12	4.5	26.7	68.8
29	Al$_2$O$_3$–Cr$_2$O$_3$	2-Methyl-2-butene	345	12	5.4	26.8	67.8
25	Al$_2$O$_3$–Fe$_2$O$_3$	2-Methyl-2-butene	347	12	3.4	28.8	67.8
69	Act. alumina	2-Methyl-2-butene	355	3	1.2	21.1	77.7
52	Act. alumina	2-Methyl-2-butene	354	6	1.9	28.0	70.1
55	Act. alumina	2-Methyl-2-butene	356	12	3.2	27.6	69.2
53	Act. alumina	2-Methyl-2-butene	356	18	3.8	27.2	69.0
59	Act. alumina	3-Methyl-1-butene	362	24	3.9	27.9	68.2
62	Act. alumina	2-Methyl-1-butene	357	12	3.8	27.2	69.0
73	Act. alumina	2-Methyl-2-butene	400	12	5.2	28.4	66.6

cause of the flatness of these plateaus compared to those in Fig. 3, it seems certain that there was no unbranching in the isomerization of the branched chain pentenes. Similar experiments showed no branching in the isomerization of the straight chain pentenes.
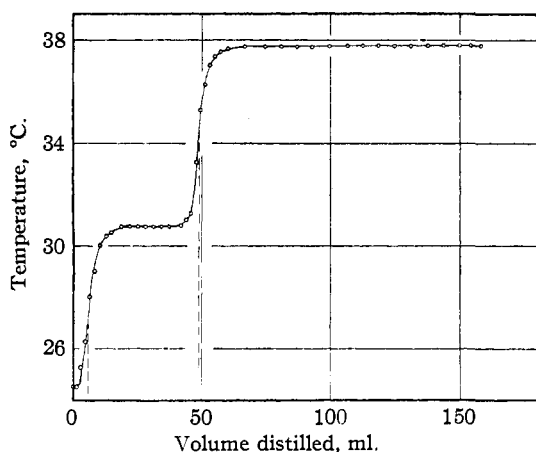

Fig. 4.—Typical distillation curve of a mixture resulting from the isomerization of 2-methyl-2-butene.

Preparation of the Pentenes.—All the pentenes used were prepared by dehydration of amyl alcohols. Tertiary amyl alcohol was dehydrated with 60% sulfuric acid to give 2-methyl-2-butene. Isoamyl alcohol and secondary butyl carbinol were dehydrated over activated alumina at 550° to give 3-methyl-1-butene and 2-methyl-1-butene, respectively. Each pentene was fractionated before subjecting it to isomerization.

Preparation of the Catalysts.—Twelve catalysts were used in this work. They were activated alumina, Al$_2$O$_3$

precipitated with ammonia, Al$_2$O$_3$ precipitated with sodium hydroxide, ThO$_2$ precipitated on pumice, CaCl$_2$, Al$_2$O$_3$ co-precipitated with 50% of SiO$_2$, with 50% of Fe$_2$O$_3$, with 25% of Cr$_2$O$_3$, MnO, CoO, NiO, or CuO.

The activated alumina was Aluminum Ore Company Grade A, 8–14 mesh. The precipitated aluminas were precipitated from solution of the nitrate, filtered, dried at 110°, washed, and dehydrated at 550°.

The ThO$_2$–pumice catalyst was prepared from thorium nitrate according to the method of Kramer and Reid.[6] The CaCl$_2$ was anhydrous, 4-mesh.

The coprecipitated catalysts of Al$_2$O$_3$ with another oxide were precipitated at the neutral point with ammonia, filtered, dried, washed, and dehydrated as described above. Water glass was used as the source of SiO$_2$, and the chlorides or nitrates of the transition metals were used.

Results

The results of isomerization of the branched chain pentenes with the different catalysts are given in Table I. The analyses are given in volume per cent. In all experiments, except those with alumina precipitated with ammonia, the flask boiled dry without raising the temperature, indicating no polymerization. The amount left in the column packing at the end of the distillation was drained and counted as the highest boiling fraction, which was 2-methyl-2-butene.

Several of the catalysts proved to be unsatisfactory for isomerization. ThO$_2$, CaCl$_2$, and alumina precipitated with sodium hydroxide produced hardly any change. Alumina precipitated with

(6) Kramer and Reid, THIS JOURNAL, **43**, 880 (1921).

ammonia, as stated before, promoted some polymerization as well as isomerization. The catalysts composed of mixtures of Al_2O_3 with SiO_2, CuO and NiO all produced a large amount of cracking, so that no reliable isomerization data could be obtained from them. Therefore the results of these catalysts are not included in the tables.

The rest of the catalysts, however, gave only isomerization and were fairly active. At *ca.* 358° for twelve hours most of these catalysts produced a mixture of approximately the same composition. At *ca.* 300° for twelve hours, however, there is considerable variation in the composition of the mixtures produced. Activated alumina (Aluminum Ore Co.) produced the greatest change at the lower temperature. Therefore this catalyst was assumed to be the best of all those tried, and it was selected as the one to be used in an attempt to establish equilibrium.

Equilibrium was obtained at four temperatures, 251, 300, 358 and 400°. Proof of equilibrium at 358° is given by (1) experiments 69, 52, 55 and 53 in which the composition of the mixture resulting from the isomerization of 2-methyl-2-butene approaches constancy with increasing time (Fig. 5), and (2) experiments 55 (or 53), 59 and 62 in which the same equilibrium mixture results from the isomerization of each of the methyl butenes. Proof of equilibrium at the other temperatures is not as complete, but it is considered probable in the light of the experiments at 358°. Equilibrium was attained in twelve hours at the three highest temperatures, but required twenty-four hours at the lowest temperature.

The average of the analyses from experiments 55, 59 and 62 at 358° is

3-Methyl-1-butene	3.6 ± 0.4
2-Methyl-1-butene	27.6 ± .4
2-Methyl-2-butene	68.8 ± .4

in terms of volume per cent. of liquid. These results provide an interesting comparison with similar data for three analogous hexenes reported by Whitmore and Meunier[7] and by Cramer and Glasebrook.[8] Their results in volume per cent. are:

	W. and M. (300°)	C. and G. (275°)
3,3-Dimethyl-1-butene	3.4	3.8
2,3-Dimethyl-1-butene	33.2	33.7
2,3-Dimethyl-2-butene	63.4	62.5

(7) Whitmore and Meunier, THIS JOURNAL, **55**, 3721 (1933).

(8) Cramer and Glasebrook, *ibid.*, **61**, 230 (1939).

These three hexenes differ from the three methylbutenes only by an extra methyl group on the number three carbon atom. The data, both on the pentenes and on the hexenes, provide support for two generalizations noted by Kistiakowsky[3] and by Ewell[9]: (1) a non-terminal double bond is a more stable structure than a terminal double bond, and (2) a chain branch adjacent to a double bond is a more stable structure than a chain branch in the saturated part of a molecule.
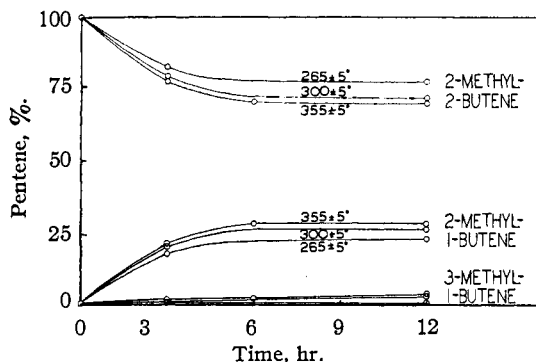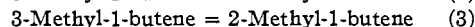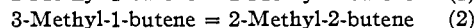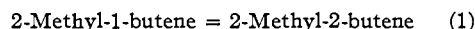

Fig. 5.—Approach to equilibrium as a function of time for the isomerization of 2-methyl-2-butene (data from Table I).

The equilibrium constants for the reactions

2-Methyl-1-butene = 2-Methyl-2-butene	(1)
3-Methyl-1-butene = 2-Methyl-2-butene	(2)
3-Methyl-1-butene = 2-Methyl-1-butene	(3)

were calculated from the analytical data by converting the volume ratios to weight ratios, and hence molar ratios, by multiplying by the densities of the pure pentenes. These equilibrium constants are given in Table II and are plotted as log K *versus* $1/T$ in Fig. 6. Several runs, which were presumed to be at equilibrium, were made at 358°, and the three points on the graph for this temperature represent the upper and lower limits and the average value. Only one run, which was presumed to be at or near equilibrium, was made at each of the other three temperatures, hence only one point is given on the graph. These data are from experiment 74 at 251°, experiment 50 at 300°, and experiment 73 at 400°. The lines on the graph are the slopes corresponding to the values of the heats of isomerization of the several reactions from Kistiakowsky's heats of hydrogenation,[3] drawn through the average value points at 358°. The agreement in reaction (1) is excellent. In reactions (2) and (3) the points at 400° appear to be low. Reactions (2) and (3) both involve 3-

(9) Ewell, *Ind. Eng. Chem.*, **32**, 778 (1940).

TABLE II

CALCULATION OF THE ENTROPIES OF ISOMERIZATION

		Reaction 1 2-methyl-1-butene = 2-methyl-2-butene	Reaction 2 3-methyl-1-butene = 2-methyl-2-butene	Reaction 3 3-methyl-1-butene = 2-methyl-1-butene
ΔH, calories (Kistiakowsky)		−1571	−3416	−1845
400° C.	K	2.37	13.3	5.6
	ΔF^0, cal.	−1155	−3465	−2305
	ΔS^0, e.u.	−0.618	0.073	0.684
358° C.	K	2.48 to 2.58	17.8 to 22.5	6.97 to 8.97
	ΔF^0, cal.	−1141 to −1191	−3620 to −3910	−2440 to −2750
	ΔS^0, e.u.	−0.681 to −0.603	0.640 to 0.784	0.944 to 1.435
300° C.	K	2.82	28.7	10.19
	ΔF^0, cal.	−1182	−3820	−2640
	ΔS^0, e.u.	−0.679	0.705	1.387
251° C.	K	3.35	41.3	12.3
	ΔF^0, cal.	−1260	−3875	−2620
	ΔS^0, e.u.	−0.594	0.876	1.480
ΔS^0, e.u. (weighted av.)		−0.64 ± 0.05	0.8 ± 0.1	1.4 ± 0.2

methyl-1-butene, and since this isomer never amounted to more than 5 or 6 ml., a small error in the fractionation analyses would make very large differences in K_2 and K_3. In view of this difficulty the nature of the agreement for these reactions must also be considered good.
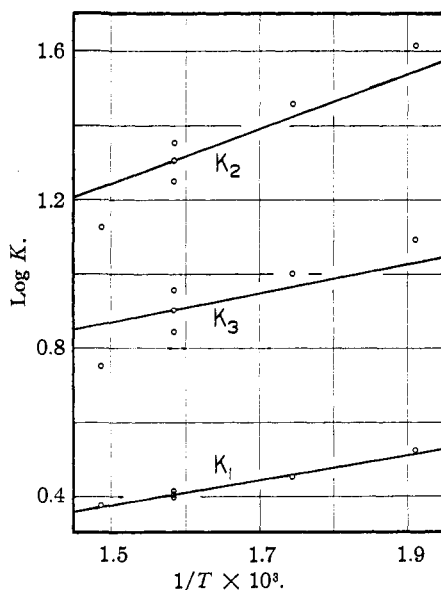

Fig. 6.—Graph of log K versus $1/T$ for reactions (1), (2) and (3). Lines are slopes corresponding to the values of the heats of isomerization of the several reactions from Kistiakowsky's heats of hydrogenation, drawn through the average value points at 358°.

Kistiakowsky's values for the heats of isomerization are used to calculate the entropies of isomerization of the several reactions, given in Table II. The heats of isomerization are as-

sumed to be independent of temperature, since the heat capacities of hydrocarbon isomers differ very little. For the same reason the entropies of isomerization should be practically independent of temperature. A range of values of ΔS^0 is given at 358°, but only one value at the other temperatures, for reasons stated above. After discarding the values for reactions (2) and (3) at 400°, the average values of ΔS^0 given at the bottom of the table were selected. Extra weight was given to the upper limit points for reactions (2) and (3) at 358°, because if the slope of Kistiakowsky's ΔH had been drawn through them, the line would have come very close to the points at the two lower temperatures. It is seen that the entropy change of reaction (3) is the arithmetic sum of the entropy changes of reactions (1) and (2). The uncertainties given the entropy values include the uncertainty in the equilibrium measurements only, and do not include that in Kistiakowsky's ΔH values. If these latter were added, the over-all uncertainties in the entropy values would, of course, be considerably larger.

Ewell[9] estimated the entropies of the pentenes using a set of rules based on data for butanes, pentanes and butenes. His estimations gave the following entropies of isomerization:

Reaction (1), $\Delta S^0 = -1.8$ e. u.
Reaction (2), $\Delta S^0 = -1.8$ e. u.
Reaction (3), $\Delta S^0 = 0$

The extent of variation from the experimental values shows how much in error such estimations may be. Provisional values for the absolute en-

tropies of the branched chain pentenes can be made if the entropy of 3-methyl-1-butene is assumed to be $S^0_{298} = 81.7$ e. u. on the basis of the following assumptions: (1) entropy of n-pentene is the entropy of n-butene plus 9.1 e. u. (the entropy difference between paraffin homologs),[10] (2) entropy of 3-methyl-1-butene is the entropy of n-pentene less the entropy difference between n-butane and isobutane[11] plus $R \ln {}^3/_2$ (correction for the difference in the symmetry numbers of n-butane and isobutane). Summarizing these assumptions:

$$S^0_{298} \text{ (3-methyl-1-butene)} = 75.4 + 9.1 - 3.6 + 0.81$$
$$= 81.7 \text{ e.u.}$$

these data being taken from Pitzer[10] and from Aston and co-workers.[11] On this basis the entropies of the branched chain pentenes are

3-Methyl-1-butene, $S^0_{298} = 81.7$ e.u.

2-Methyl-1-butene, $S^0_{298} = 83.1$ e.u.

2-Methyl-2-butene, $S^0_{298} = 80.4$ e.u.

Isomerization of the n-Pentenes.—A similar set of experiments was made on the isomerization of the straight chain pentenes. The results are not of much value because the cis- and trans-isomers of 2-pentene could not be separated accurately with the fractionating columns used. However, a brief description of the experiments and results will be given.

The same apparatus and catalysts were used as above. The 1-pentene was prepared by dehydration of n-amyl alcohol over activated alumina at 550°. The 2-pentene was prepared by dehydration of diethylcarbinol with 65% sulfuric acid, and the product was probably a mixture of the cis and trans isomers.

The results are summarized in Table III. Two noteworthy results are observed: (1) most of the catalysts produced approximately the same

(10) Pitzer, Chem. Rev., **27**, 39 (1940).

(11) Aston and Messerly, THIS JOURNAL, **62**, 1917 (1940); Aston, Kennedy and Schumann, ibid., **62**, 2059 (1940).

amount of isomerization of 2-pentene, namely, 10–15%, and (2) the single experiment on 1-pentene produced practically the same mixture as did the experiments on 2-pentene, and probably would have produced the same mixture within the analytical error if a longer time had been allowed.

TABLE III

ISOMERIZATION OF STRAIGHT CHAIN PENTENES

Expt.	Catalyst	Starting material	Temp., °C.	Time, hr.	Composition of product, volume, %	
					1-Pentene	2-Pentene
67	Act. alumina	2-Pentene	266	3	1.9	98.1
31	Al₂O₃–CoO	2-Pentene	320	12	4.6	95.4
41	Al₂O₃–MnO	2-Pentene	305	12	10.7	89.3
49	Al₂O₃–MnO	2-Pentene	301	12	9.4	90.6
28	Al₂O₃–Cr₂O₃	2-Pentene	295	12	11.8	88.2
24	Al₂O₃–Fe₂O₃	2-Pentene	295	12	6.9	93.1
54	Act. alumina	2-Pentene	300	6	8.1	91.9
64	Act. alumina	2-Pentene	299	12	9.4	90.6
33	Al₂O₃–CoO	2-Pentene	375	12	13.6	86.4
44	Al₂O₃–MnO	2-Pentene	366	12	15.5	84.5
46	Al₂O₃–MnO	2-Pentene	362	12	15.4	84.6
30	Al₂O₃–Cr₂O₃	2-Pentene	345	12	13.4	86.6
26	Al₂O₃–Fe₂O₃	2-Pentene	344	12	10.6	89.4
61	Act. alumina	2-Pentene	358	3	10.0	90.0
58	Act. alumina	2-Pentene	359	6	14.5	85.5
51	Act. alumina	2-Pentene	358	12	15.8	84.2
56	Act. alumina	2-Pentene	364	18	15.3	84.7
68	Act. alumina	1-Pentene	357	12	21.9	78.1

Summary

1. Equilibrium in the vapor phase among the branched chain pentenes has been established at four temperatures. The analyses of the equilibrium mixtures were carried out by fractional distillation.

2. Combination of the equilibrium constants for the isomerization reactions with the heats of isomerization calculated from Kistiakowsky's heats of hydrogenation gives the following entropy differences between the isomers:

2-Methyl-1-butene (g) = 2-methyl-2-butene (g),
$$\Delta S^0 = -0.64 \pm 0.05 \text{ e.u.}$$
3-Methyl-1-butene (g) = 2-methyl-2-butene (g),
$$\Delta S^0 = 0.8 \pm 0.1 \text{ e.u.}$$
3-Methyl-1-butene (g) = 2-methyl-1-butene (g),
$$\Delta S^0 = 1.4 \pm 0.2 \text{ e.u.}$$