HEATS OF ISOMERIZATION OF THE NINE HEPTANES

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ABSTRACT

The heats of isomerization of all of the nine heptanes except 2-methylhexane
and 3-methylhexane were determined by measurement of the ratios of their
heats of combustion in the liquid state, using the procedure previously described
for the hexanes. Values for 2-methylhexane and 3-methylhexane were calculated
from the corresponding experimental values for the isomerization of n-hexane
into 2-methylpentane and 3-methylpentane and of n-octane into 2-methylheptane
and 3-methylheptane, respectively.

The following values were obtained for the liquid state at 25° C, and were
calculated to the gaseous state at 25° C and 0° K:

	Heat of isomerization, ΔH, for n-C_7H_{16}=i-C_7H_{16}		
Isomer	Liquid	Gas	
	25° C	25° C	0° K
	kcal/mole	*kcal/mole*	*kcal/mole*
n-Heptane	0	0	0
2-Methylhexane	−1.30 ±0.25	−1.80 ±0.29	−1.21 ±0.31
3-Methylhexane	−0.72 ±0.25	−1.18 ±0.29	−0.42 ±0.31
3-Ethylpentane	−.14 ±0.23	−0.52 ±0.27	+.48 ±0.30
2,2-Dimethylpentane	−3.42 ±0.28	−4.45 ±0.32	−3.40 ±0.34
2,3-Dimethylpentane	−2.18 ±0.26	−2.80 ±0.30	−1.71 ±0.32
2,4-Dimethylpentane	−2.54 ±0.16	−3.40 ±0.22	−2.32 ±0.25
3,3-Dimethylpentane	−2.44 ±0.15	−3.24 ±0.21	−2.23 ±0.24
2,2,3-Trimethylbutane	−3.00 ±0.22	−4.17 ±0.27	−3.02 ±0.30

CONTENTS

I. INTRODUCTION

In continuation of the program of determining the heats of formation
and of isomerization of the paraffin hydrocarbons [1, 2],[1] calorimetric

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[1] Figures in brackets indicate the literature references at the end of this paper. References to all the
earlier papers are given in [1].

measurements have been made which yield values for the differences in the heats of combustion of all of the nine heptanes, except 2-methylhexane and 3-methylhexane, for the liquid state at 25° C. Values for the latter two, in reference to n-heptane, were determined from the corresponding values for the differences in the heats of combustion of n-hexane, 2-methylpentane, and 3-methylpentane, the data for which have already been published [2], and of n-octane, 2-methylheptane and 3-methylheptane, which have been determined but not yet published [3]. These values for the differences in the heats of combustion, which are also the heats of isomerization in the liquid state at 25° C, have been combined with calculated values for the differences in the heats of vaporization to give values for the heats of isomerization in the gaseous state at 25° C. Combination of these with values for the decrease in heat content of the various isomers in the gaseous state from 25° C to 0° K gives values for the heats of isomerization for the ideal gaseous state at 0° K.

II. UNIT OF ENERGY, MOLECULAR WEIGHTS, ETC.

The unit of energy upon which the values reported in this paper are based is the International joule. For conversion to the conventional artificial, or defined, calorie, the following relation is used [1]:

$$4.1833 \text{ International joules} = 1 \text{ calorie.}$$

The molecular weight of carbon dioxide, the mass of which was used to determine the amount of reaction, was taken as 44.010, from the 1941 table of atomic weights [4].

The uncertainties assigned to the various quantities dealt with in this paper were derived, where possible, by a method previously described [5].

Definitions of all the symbols used are given in the previous publication [2].

III. METHOD AND APPARATUS

The same method and apparatus were used in the present investigation as in the work on the hexanes [2].

IV. EXPERIMENTAL PROCEDURES

1. CHEMICAL

The description of the heptanes investigated is as follows:

n-Heptane.—Relatively pure n-heptane, prepared commercially [2] for use as an automotive antiknock standard, was further purified by distillation in a column having a separating efficiency equivalent to about 100 theoretical plates [6], with subsequent filtration through silica gel [9]. The purified material contained 0.0012 ±0.0002 mole fraction of impurity as determined by A. R. Glasgow, Jr., of the API Research Project 6 at this Bureau, from time-temperature freezing curves [7].

3-Ethylpentane.—This isomer was synthetic material prepared and purified at this Bureau by Brooks, Howard, and Crafton [8], who have described its preparation, purification, and properties. While

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[2] Carbide and Carbon Chemicals Corp., New York, N. Y.

these authors did not make a quantitative determination of the amount of impurity in this material, the nature of the distillation and freezing curves indicated it to be one of their purer compounds. Before use in the present investigation, the material was filtered through silica gel [9].

2,2-Dimethylpentane and 3,3-dimethylpentane.—These isomers were obtained by the further purification of material synthesized by Soroos and Willis [11] and kindly made available for this investigation by George Callingaert of the Ethyl Gasoline Corporation, Detroit, Mich. The additional purification consisted in azeotropic distillation with methyl alcohol [10] through a column having a separating efficiency equivalent to about 140 theoretical plates [6], with subsequent filtration through silica gel [9]. The purified materials contained the following amounts of impurity, as determined by A. R. Glasgow, Jr., from time-temperature freezing and melting curves [7]: 2,2-dimethylpentane, 0.0015 ±0.0005 mole fraction; 3,3-dimethylpentane, 0.0003 ±0.0002 mole fraction.

2,3-Dimethylpentane and 2,4-dimethylpentane.—These isomers were from synthetic material prepared and purified by the section on Automotive Power Plants at this Bureau [12]. Before use, the hydrocarbons were filtered through silica gel [9]. No quantitative determination was made of the amount of impurity in either of these two compounds. For 2,4-dimethylpentane, the nature of the distillation and freezing curves indicated it to be of a purity comparable to that of the 3-ethylpentane described above [12]. The 2,4-dimethylpentane had a freezing point in air at 1 atm of −119.86° C [12], and the amount of impurity in it was estimated to be 0.006 ±0.004 mole fraction. For 2,3-dimethylpentane, no freezing curves were obtained, and the nature of the distillation curve indicated it to be of a lesser purity than the 2,4-dimethylpentane [12]. The amount of impurity in the 2,3-dimethylpentane was estimated to be 0.03 ±0.02 mole fraction.

2, 2, 3-Trimethylbutane.—This isomer was synthetic material kindly placed at our disposal by George Callingaert of the Ethyl Gasoline Corporation, Detroit, Mich. It was further purified by crystallization with centrifuging, with subsequent filtration through silica gel [9]. The purified material contained 0.009 ±0.002 mole fraction of impurity, as determined by A. R. Glasgow, Jr., from time-temperature freezing curves [7].

It is important to note that the heptanes used were so prepared and purified that the residual impurities must have consisted largely of isomeric heptanes. Further, the impurities would be only those having boiling points near that of the given isomer. The values given in table 1 indicate the olerances with regard to such impurities, and also the actual amounts of impurity. From these data it appears that the amounts of impurity in each of the seven heptanes investigated were not sufficient to affect significantly their heats of combustion.

The procedures for sealing the hydrocarbons in glass ampoules, purifying the oxygen used for combustion, igniting the hydrocarbon, examining the products of combustion, and determining the amount of reaction have been described previously [2].

2. CALORIMETRIC

The calorimetric procedure was the same as that in the work on the hexanes [2].

V. RESULTS

The experimental results of the present investigation are presented in tables, 2, 3, 4, 5, 6, 7, and 8, which give the data yielding values of B in ohms per gram of carbon dioxide, as defined by eq 4 of the previous paper [2], for n-heptane, 3-ethylpentane, 2,2-dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethyl pentane, and 2,2,3-trimethylbutane, respectively, in the liquid state at 28° C. The symbols have the same significance as in the previous paper [2]. The value of the heat of isomerization was obtained by means of the relation [2]:

$$(-\Delta U_B)_n - (-\Delta U_B)_i = (-\Delta U_B)_n (1 - B_i/B_n).$$

For this calculation the value of $(-\Delta U_B)_n$ was taken as 4,803 kj/mole [13].

TABLE 1.—*Tolerances of the amounts of close-boiling isomeric impurities in the heptanes*

Compound	Possible major impurities	Amount of each such impurity required to change the heat of combustion by 5 parts in 100,000	Amount of impurity in the material used in this work
		Mole fraction	*Mole fraction*
n-Heptane			0.0012 ±0.0002
3-Ethylpentane	{ 3-methylhexane	0.10	} ᵃ.006 ±0.004
	2-methylhexane	.05	
2, 3-Dimethylpentane	2-methylhexane	.07	ᵃ.03 ±0.02
3, 3-Dimethylpentane	2, 3-dimethylpentane	.22	.0003 ±0.0002
2, 2, 3-Trimethylbutane	{ 2, 2-dimethylpentane	.14	} .009 ±0.002
	2, 4-dimethylpentane	.13	
2, 4-Dimethylpentane	{ 2, 2-dimethylpentane	.07	} ᵃ.006 ±0.004
	2, 2, 3-trimethylbutane	.13	
2, 2-Dimethylpentane	{ 2, 4-dimethylpentane	.07	} .0015 ±0.0005
	2, 2, 3-trimethylbutane	.14	

ᵃ Estimate, not determined quantitatively.

TABLE 2.—*n-Heptane*

Experiment	Mass of carbon dioxide formed	k	K	U	ΔR_c	Δr_i	Δr_n	B^a	Deviation from mean
	g	*min⁻¹*	*Ohms*	*Ohms*	*Ohms*	*Ohms*	*Ohms*	*Ohms/g CO₂*	*Ohms/g CO₂*
1	2.69665	0.001955	0.000742	0.000413	0.305524	0.000423	0.000093	0.1130802	−0.0000051
2	2.71804	.001961	.000709	.000422	.307941	.000415	.000092	.1130829	−.0000024
3	2.33331	.001956	.001875	.000349	.264397	.000417	.000078	.1130689	−.0000164
4	2.20202	.001960	.002310	.000368	.249606	.000415	.000077	.1130946	.0000093
5	2.40038	.001948	.001678	.000342	.272024	.000414	.000043	.1131031	.0000178
6	2.22713	.001954	.002238	.000278	.252448	.000434	.000039	.1131036	.0000183
7	2.37067	.001964	.001771	.000408	.268559	.000404	.000041	.1130639	−.0000214
Mean								0.1130853	
Standard deviation of the mean								±0.0000060	

ᵃ Corrected to the standard calorimetric system and to 28.00° C.

TABLE 3.—*3-Ethylpentane*

Experiment	Mass of carbon dioxide formed	k	K	U	ΔR_c	Δr_i	Δr_n	B^a	Deviation from mean
	g	*min⁻¹*	*Ohms*	*Ohms*	*Ohms*	*Ohms*	*Ohms*	*Ohms/g CO₂*	*Ohms/g CO₂*
1	2.44412	0.001956	0.001499	0.000638	0.267877	0.000412	0.000081	0.1130525	−0.0000191
2	2.55514	.001951	.001121	.000640	.289438	.000412	.000086	.1130552	−.0000164
3	2.62973	.001960	.000288	.000578	.297910	.000412	.000089	.1130721	.0000005
4	2.30390	.001952	.001916	.000627	.261095	.000417	.000077	.1130805	.0000089
5	2.39864	.001937	.001627	.000558	.271849	.000413	.000082	.1130975	.0000259
Mean								0.1130716	
Standard deviation of the mean								±0.0000083	

ᵃ Corrected to the standard calorimetric system and to 28.00° C.

TABLE 4.—*2,2-Dimethylpentane*

Experiment	Mass of carbon dioxide formed	k	K	U	ΔR_c	Δr_i	Δr_n	B^a	Deviation from mean
	g	*min⁻¹*	*Ohms*	*Ohms*	*Ohms*	*Ohms*	*Ohms*	*Ohms/g CO₂*	*Ohms/g C₂*
1	2.59807	0.001962	0.001113	0.000347	0.293569	0.000429	0.000087	0.1127684	0.0000199
2	2.57774	.001957	.001169	.000350	.291268	.000413	.000081	.1127734	.0000249
3	2.61289	.001957	.001039	.000317	.295146	.000415	.000080	.1127523	.0000038
4	2.29817	.001949	.001868	.000363	.259599	.000422	.000041	.1127243	−.0000242
5	2.77610	.001953	.000578	.000344	.313468	.000418	.000048	.1127240	−.0000245
Mean								0.1127485	
Standard deviation of the mean								±0.0000105	

ᵃ Corrected to the standard calorimetric system and to 28.00° C.

TABLE 5.—*2,3-Dimethylpentane*

Experiment	Mass of carbon dioxide formed	k	K	U	ΔR_c	Δr_i	Δr_n	B^a	Deviation from mean
	g	*min⁻¹*	*Ohms*	*Ohms*	*Ohms*	*Ohms*	*Ohms*	*Ohms/g CO₂*	*Ohms/g CO₂*
1	2.71689	0.001956	0.000723	0.000381	0.307129	0.000415	0.000092	0.1128330	−0.0000365
2	2.66418	.001957	.000846	.000374	.301333	.000410	.000088	.1128927	.0000232
3	2.80302	.001964	.000368	.000443	.316925	.000407	.000093	.1128642	−.0000053
4	2.20959	.001956	.002290	.000398	.249934	.000411	.000080	.1128553	−.0000142
5	2.16932	.001944	.002401	.000360	.245448	.000425	.000073	.1128792	.0000097
6	2.41740	.001935	.001547	.000277	.273440	.000416	.000042	.1128924	.0000229
Mean								0.1128695	
Standard deviation of the mean								±0.0000095	

ᵃ Corrected to the standard calorimetric system and to 28.00° C.

TABLE 6.—2,4-Dimethylpentane

Experiment	Mass of carbon dioxide formed	k	K	U	ΔR_j	Δr_i	Δr_n	B^a	Deviation from mean
	g	min^{-1}	$Ohms$	$Ohms$	$Ohms$	$Ohms$	$Ohms$	$Ohms/g\ CO_2$	$Ohms/g\ CO_2$
1	2.56395	0.001960	0.001233	0.000326	0.289884	0.000407	0.000091	0.1128400	0.0000046
2	2.41832	.001963	.001654	.000315	.273421	.000409	.000080	.1128303	−.0000051
3	2.54547	.001951	.001234	.000397	.287796	.000415	.000088	.1128366	.0000012
4	2.58308	.001954	.001113	.000368	.292052	.000409	.000086	.1128449	.0000095
5	2.26723	.001955	.002120	.000306	.256334	.000415	.000041	.1128250	−.0000104

Mean_____ 0.1128354 _____

Standard deviation of the mean_____ ±0.0000035 _____

^{a} Corrected to the standard calorimetric system and to 28.00° C.

TABLE 7.—3,3-Dimethylpentane

Experiment	Mass of carbon dioxide formed	k	K	U	ΔR_e	Δr_i	Δr_n	B^a	Deviation from mean
	g	min^{-1}	$Ohms$	$Ohms$	$Ohms$	$Ohms$	$Ohms$	$Ohms/g\ CO_2$	$Ohms/g\ CO_2$
1	2.82133	0.001954	0.000326	0.000557	0.318930	0.000413	0.000095	0.1128396	−0.0000043
2	2.73915	.001948	.000622	.000578	.309675	.000418	.000092	.1128445	.0000006
3	2.78168	.001956	.000479	.000549	.314480	.000412	.000105	.1128445	.0000006
4	2.76041	.001958	.000552	.000592	.312089	.000414	.000095	.1128505	.0000066
5	2.69239	.001958	.000702	.000438	.304380	.000413	.000089	.1128403	−.0000036

Mean_____ 0.1128439 _____

Standard deviation of the mean_____ ±0.0000019 _____

^{a} Corrected to the standard calorimetric system and to 28.00° C.

TABLE 8.—2,2,3-Trimethylbutane

Experiment	Mass of carbon dioxide formed	k	K	U	ΔR_c	Δr_i	Δr_n	B^a	Deviation from mean
	g	min^{-1}	$Ohms$	$Ohms$	$Ohms$	$Ohms$	$Ohms$	$Ohms/g\ CO_2$	$Ohms/g\ CO_2$
1	2.26429	0.001947	0.002065	0.000101	0.255903	0.000417	0.000077	0.1128059	0.0000170
2	2.53725	.001948	.001127	.000131	.286617	.000406	.000083	.1127835	−.0000054
3	2.70182	.001945	.000506	.000173	.305223	.000411	.000092	.1127990	.0000101
4	2.55395	.001946	.001131	.000099	.288454	.000408	.000091	.1127628	−.0000261
5	2.39197	.001962	.001677	.000368	.270370	.000414	.000043	.1128087	.0000198
6	2.57436	.001959	.001155	.000362	.290854	.000415	.000044	.1127736	−.0000153

Mean_____ 0.1127889 _____

Standard deviation of the mean_____ ±0.0000076 _____

^{a} Corrected to the standard calorimetric system and to 28.00° C.

TABLE 9.—*Heats of isomerization of the heptanes in the liquid state* [a]

Substance	B at 28.00° C	Ratio of the heats of combustion in the bomb process B_i/B_n at 28° C	Difference in the heats of combustion in the bomb process [b] $(-\Delta U_B)_n - (-\Delta U_B)_i$ at 28° C	Heat of isomerization of the liquid H_i° (liq) $- H_n^\circ$ (liq) at 25° C	
	Ohms/g CO_2		*kj/mole*	*kj/mole*	*kcal/mole*
n-Heptane	0.1130853 ±0.0000120	1.000000	0.00	0.00	0.00
2-Methylhexane					−1.30 ±0.25
3-Methylhexane					−0.72 ±0.25
3-Ethylpentane	.1130716 ±0.0000166	.999879 ±0.000205	0.58 ±0.98	−0.57 ±0.98	−.14 ±0.23
2,2-Dimethylpentane	.1127485 ±0.0000210	.997022 ±0.000242	14.30 ±1.16	−14.29 ±1.16	−3.42 ±0.28
2,3-Dimethylpentane	.1128695 ±0.0000190	.998092 ±0.000225	9.16 ±1.08	−9.14 ±1.08	−2.18 ±0.26
2,4-Dimethylpentane	.1128354 ±0.0000070	.997790 ±0.000139	10.61 ±0.67	−10.61 ±0.67	−2.54 ±0.16
3,3-Dimethylpentane	.1128439 ±0.0000038	.997865 ±0.000126	10.25 ±0.61	−10.22 ±0.61	−2.44 ±0.15
2,2,3-Trimethylbutane	.1127889 ±0.0000152	.997379 ±0.000194	12.59 ±0.93	−12.56 ±0.93	−3.00 ±0.22

[a] All the uncertainties assigned to the experimental quantities in this table are equal to twice the standard deviation [5]. The uncertainty to be assigned to the value of the heat of isomerization of any one of the isomers into any other one may conservatively be taken, on the average, as ±0.25 kcal/mole.
[b] Obtained by subtracting the value in column 3 from unity and multiplying with the factor 4,803 kj/mole (see section VI).

TABLE 10.—*Heats of isomerization of the nine heptanes in the gaseous state* [a]

Substance	Heat of isomerization of the liquid H_i° (liq) $- H_n^\circ$ (liq) at 25° C		Difference in the heats of vaporization $(\Delta H_{vap}^\circ)_n - (\Delta H_{vap}^\circ)_i$ at 25° C	Heat of isomerization of the gas H_i° (g) $- H_n^\circ$ (g) at 25° C	$(H_{298}^\circ - H_0^\circ)_n - (H_{298}^\circ - H_0^\circ)_i$	Heat of isomerization of the gas H_i° (g) $- H_n^\circ$ (g) at 0° K
	kj/mole	*kcal/mole*	*kcal/mole*	*kcal/mole*	*kcal/mole*	*kcal/mole*
n-Heptane	0	0	0	0	0	0
2-Methylhexane		−1.30 ±0.25	0.50 ±0.15	−1.80 ±0.29	0.59 ±0.12	−1.21 ±0.31
3-Methylhexane		−0.72 ±0.25	.46 ±0.15	−1.18 ±0.29	.76 ±0.12	−.42 ±0.31
3-Ethylpentane	−0.57 ±0.98	−.14 ±0.23	.38 ±0.15	−.52 ±0.27	1.00 ±0.12	+.48 ±0.30
2,2-Dimethylpentane	−14.29 ±1.16	−3.42 ±0.28	1.03 ±0.15	−4.45 ±0.32	1.05 ±0.12	−3.40 ±0.34
2,3-Dimethylpentane	−9.14 ±1.08	−2.18 ±0.26	0.62 ±0.15	−2.80 ±0.30	1.09 ±0.12	−1.71 ±0.32
2,4-Dimethylpentane	−10.61 ±0.67	−2.54 ±0.16	.86 ±0.15	−3.40 ±0.22	1.08 ±0.12	−2.32 ±0.25
3,3-Dimethylpentane	−10.22 ±0.61	−2.44 ±0.15	.80 ±0.15	−3.24 ±0.21	1.01 ±0.12	−2.23 ±0.24
2,2,3-Trimethylbutane	−12.56 ±0.93	−3.00 ±0.22	1.17 ±0.15	−4.17 ±0.27	1.15 ±0.12	−3.02 ±0.30

[a] The uncertainty to be assigned to the value of the heat of isomerization of any one of the isomers into any other one may be taken as ±0.25 kcal/mole for the liquid at 25° C, ±0.29 kcal/mole for the gas at 25°C, and ±0.31 kcal/mole for the gas at 0°K.

TABLE 11.—Comparison of the three sets of data on the heats of isomerization of the nine heptanes in the liquid state at 25° C

Isomer	H_i^o (liq)$-H_n^o$ (liq) at 25° C		
	Present work	Jessup [16][a]	Davies and Gilbert [17][a]
	kcal/mole	kcal/mole	kcal/mole
n-Heptane	0	0	0
2-Methylhexane	−1.30 ±0.25	−1.4 ±1.0	−1.25 ±0.40
3-Methylhexane	−0.72 ±0.25	−0.8 ±1.0	−0.52 ±0.50
3-Ethylpentane	−.14 ±0.23	+.1 ±1.0	−.19 ±0.40
2,2-Dimethylpentane	−3.42 ±0.28	−3.6 ±1.0	−3.91 ±0.40
2,3-Dimethylpentane	−2.18 ±0.26	−1.2 ±1.0	−1.70 ±0.40
2,4-Dimethylpentane	−2.54 ±0.16	−1.2 ±1.0	−2.99 ±0.40
3,3-Dimethylpentane	−2.44 ±0.15	−2.2 ±1.0	−3.03 ±0.50
2,2,3-Trimethylbutane	−3.00 ±0.22	−2.5 ±1.0	−2.80 ±0.30

[a] See text for discussion of these values.

In table 9 are given, for the seven isomeric heptanes investigated, values for the following: the constant B in ohms per gram of carbon dioxide, as given in tables 2 to 8, inclusive; the ratio of the heat evolved, per mole of hydrocarbon, in the bomb process at 28° C for each isomer to that for n-heptane; the difference, between n-heptane and each isomer, in the heat of combustion in the bomb process at 28° C; and the heat of isomerization, for the liquid state at 25° C and 1 atm, of n-heptane into each isomer. Values for the last-named property are also given in the last column of table 9 for 2-methyl-hexane and 3-methylhexane. These were obtained in the following way:

In the previous paper [2], the heat of isomerization of n-hexane into 2-methylpentane and 3-methylpentane, respectively, for the liquid state at 25° C and 1 atm, were determined to be −1.30 ±0.21 and −0.76 ±0.19 kcal/mole. Unpublished data obtained by the authors yield for the heats of isomerization of n-octane into 2-methylheptane and 3-methylheptane, respectively, for the liquid state at 25° C and 1 atm, the values −1.50 ±0.30 and −0.63 ±0.30 kcal/mole. The values for the heat of isomerization of n-heptane into 2-methylhexane and 3-methylhexane, respectively, for the liquid state at 25° C and 1 atm, were taken as the weighted means of the corresponding values for the analogous hexanes and octanes.

In table 10 are given values for the following: the heat of isomerization, for the liquid state at 25° C, of n-heptane into each isomer, as given in table 9; the difference, between n-heptane and each isomer, in the heat of vaporization at 25° C for the gas in the ideal state [14]; the heat of isomerization, for the ideal gaseous state, of n-heptane into each isomer at 25° C; the difference, between n-heptane and each isomer, in the value of $H_{298}^o-H_0^o$, the heat content at 298° K referred to the absolute zero, for the ideal gaseous state [18]; and, finally, the heat of isomerization, for ideal gaseous state, of n-heptane into each isomer at 0° K.

VI. DATA OF PREVIOUS INVESTIGATIONS

Prior to 1941 the only published works on the determination of the heats of combustion for any of the heptanes were those of Louguinine [15] and Jessup [13], each of whom measured n-heptane only. There

are available to the authors, however, two sets of data involving the nine isomeric heptanes, which may be compared with the results of the present investigation.

The first set of such values are from some unpublished data obtained by Jessup [16] at this Bureau in 1927, in an investigation in which circumstances made it possible to perform only two combustion experiments on each of eight isomers and three on the remaining one. In a number of these experiments, a significant amount of carbon remained unburned. Because of the then unavoidable limitations placed upon these experiments of Jessup, the values of the heats of isomerization deduced from the unpublished data that he has kindly placed at our disposal are arbitrarily assigned an uncertainty of ± 1.0 kcal/mole. These values are shown in table 11 in comparison with the present values.

The second set of data available for comparison are those recently obtained by Davies and Gilbert [17]. In their investigation, the purity of the isomers was not determined quantitatively, and the amount of reaction was in each case computed from the mass of liquid placed in the bomb. The values of the heats of isomerization obtained from their data are shown in table 11 in comparison with the values from the present investigation. The uncertainties are those assigned by Gilbert in a private communication to the authors.

All of the values given in table 11 are substantially in accord, within their assigned limits of uncertainty.

VII. DISCUSSION

As has been previously pointed out, values of the heats of isomerization of the heptanes, along with those of the other paraffin hydrocarbons, are needed in studying the influence of structure upon the energy content of the molecule and in calculating, in combination with entropies or the free energy functions, values of the free energies of isomerization.

With regard to the correlation of the energy content with structure, it is planned to report the results of such a study after the heats of isomerization of the 18 octanes, and perhaps 1 or 2 selected nonanes, have been determined. For the present, it may be sufficient to point out that the data reported here on the heats of isomerization of the heptanes follow the generalization already made by one of the authors [1] concerning the change with structure of the energy content of isomeric hydrocarbons. This generalization may be stated as follows: With regard to energy content, the stability of the molecule increases with increase in the compactness of the carbon skeleton, up to the point where too close proximity of the hydrogen atoms on different carbon atoms produces a decrease in the stability of the molecule. The most stable isomer, with regard to energy content, appears to be that one which has a maximum of compactness and at the same time has the hydrogen atoms so disposed as to interfere little with one another. This is illustrated by the fact that the 2,2-dimethyl isomer is uniformly the most stable at 0° K, and that the 3-methyl and 3-ethyl isomers are the least stable of the branched chain isomers. It may also be noted that, at 0° K, 2,2-dimethylpentane appears to be slightly more stable than the more highly branched isomer, 2,2,3-trimethylbutane, and definitely more stable than 3,3-dimethylpentane.

Substitution on the 3- position tends to produce instability because of interference among the hydrogen atoms.

Research Paper RP1440 [19] illustrates the use of the data on heats of isomerization reported here in calculating free energies of isomerization.

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