A side reaction indicating apparent steric hindrance in the formation of certain cyclic compounds has been studied.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

THERMAL DATA ON ORGANIC COMPOUNDS. VIII. THE HEAT CAPACITIES, ENTROPIES AND FREE ENERGIES OF THE ISOMERIC HEPTANES[1]

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Recently the nine isomeric heptanes have been prepared in a very pure form by Edgar, Calingaert and Marker.[5] Various physical properties of these samples were subsequently studied by a number of investigators, and much of the resulting data has been discussed and summarized by Edgar and Calingaert.[6] Through the courtesy of Dr. Edgar we have enjoyed the privilege of measuring the heat capacities of these isomers from liquid air temperatures up to that of the room. From the data thus obtained, the corresponding entropies and free energies have been calculated by means of the third law of thermodynamics. The present paper gives the results of our investigation.

In an earlier study dealing with a few isomeric organic compounds, two of us[7] suggested that "in the case of isomers the compound with the lowest melting point has the largest entropy and free energy." The present investigation, as well as the data recently obtained for three isomeric octanes,[8] does not support this suggestion. Rather it appears that in a group of isomers the entropy decreases systematically as the amount of branching increases. Thus the normal compound has always been found to have the largest entropy value. However, in the case of two isomers involving equal amounts of branching, it is usually true that the compound with the lower melting point has the larger entropy. At present no rule

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[1] This paper contains results obtained in an investigation of the heat capacities and free energies of some typical hydrocarbon compounds, listed as Project No. 29 of the American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by The Universal Oil Products Company. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

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[5] Edgar, Calingaert and Marker, THIS JOURNAL, **51**, 1483 (1929).

[6] Edgar and Calingaert, *ibid.*, **51**, 1540 (1929).

[7] Parks and Huffman, *ibid.*, **48**, 2788 (1926).

[8] Parks, Huffman and Thomas, *ibid.*, **52**, 1032 (1930).

concerning the free energy of formation of isomers appears universally applicable to all the hydrocarbons and alcohols that have been studied.

Experimental Results

In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats and the fusion data. The apparatus and details of experimental procedure have been fully described in other places.[9] In view of the accuracy of the various measurements involved and the purity of the several heptane samples, the error in the experimental values is probably less than 1%.

Table I

Specific Heats

	No. 3. 3-Methylhexane: Glass and liquid							
Temp., °K.	71.1	74.7	78.0	81.1	84.0	86.9	89.2	
C_p per g.	0.178	0.187	0.197	0.205	0.215	0.240	0.362	
Temp., °K.	91.0	92.8	95.1	99.1	106.3	118.9	131.4	
C_p per g.	0.395	0.397	0.398	0.398	0.400	0.403	0.407	
Temp., °K.	151.8	173.8	195.7	219.8	243.1	275.8	289.2	
C_p per g.	0.415	0.426	0.440	0.457	0.472	0.498	0.511	
	No. 4. 3-Ethylpentane: Crystals							
Temp., °K.	92.2	98.3	105.0	112.1	118.9	125.2	131.4	137.2
C_p per g.	0.206	0.216	0.227	0.238	0.248	0.259	0.269	0.282
	Liquid							
Temp., °K.	161.4	166.8	180.4	200.2	217.5	237.5	258.5	
C_p per g.	0.416	0.419	0.427	0.442	0.455	0.470	0.486	
Temp., °K.	275.4	282.2	287.5	294.8				
C_p per g.	0.499	0.505	0.510	0.519				
	No. 5. 2,2-Dimethylpentane: Crystals							
Temp., °K.	91.9	97.9	103.3	103.3	111.2	118.4	124.9	131.0
C_p per g.	0.200	0.210	0.219	0.219	0.234	0.249	0.265	0.281
	Liquid							
Temp., °K.	153.2	154.3	162.2	177.5	186.1	199.8	215.8	
C_p per g.	0.388	0.389	0.395	0.407	0.415	0.428	0.442	
Temp., °K.	237.4	256.8	275.1	275.1	281.3	287.2	294.1	
C_p per g.	0.461	0.478	0.498	0.497	0.505	0.511	0.518	
	No. 6. 2,3-Dimethylpentane: Glass and liquid							
Temp., °K.	68.4	72.8	76.8	80.7	83.3	84.1	86.8	86.9
C_p per g.	0.169	0.177	0.189	0.205	0.252	0.253	0.377	0.377
Temp., °K.	89.2	90.4	92.1	94.2	104.7	111.3	128.0	133.9
C_p per g.	0.376	0.374	0.374	0.376	0.380	0.383	0.389	0.393
Temp., °K.	160.3	181.5	205.0	210.8	234.0	240.1	277.2	291.3
C_p per g.	0.409	0.421	0.437	0.442	0.459	0.465	0.496	0.510

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[9] Parks, This Journal, 47, 338 (1925); also Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

TABLE I (*Concluded*)

No. 7. 2,4-Dimethylpentane: Crystals

Temp., °K.	91.6	95.1	97.4	104.2	111.6	120.0	129.8	136.3
C_p per g.	0.201	0.209	0.212	0.223	0.237	0.254	0.284	0.313

Liquid

Temp., °K.	160.2	161.2	171.7	181.4	196.3	205.7	215.3	225.7
C_p per g.	0.400	0.402	0.410	0.417	0.430	0.440	0.449	0.458
Temp., °K.	236.4	242.4	261.4	275.4	281.5	288.1	294.4	
C_p per g.	0.468	0.472	0.493	0.505	0.512	0.519	0.527	

No. 8. 3,3-Dimethylpentane: Crystals

Temp., °K.	92.3	97.5	103.7	108.7	114.0	118.2	123.0	128.5
C_p per g.	0.192	0.201	0.212	0.223	0.233	0.243	0.254	0.272

Liquid

Temp., °K.	145.7	151.4	160.7	171.9	183.0	195.5	210.5	225.7
C_p per g.	0.392	0.395	0.400	0.405	0.412	0.421	0.432	0.444
Temp., °K.	239.9	252.7	275.1	280.3	286.5	292.9		
C_p per g.	0.456	0.466	0.486	0.492	0.498	0.505		

No. 9. 2,2,3-Trimethylbutane: Crystals I

Temp., °K.	89.5	92.2	94.8	96.7	97.4	99.7	102.8	103.9
C_p per g.	0.212	0.222	0.232	0.242	0.246	0.261	0.330	0.356
Temp., °K.	108.0	109.3	112.2	116.3				
C_p per g.	0.299	0.294	0.298	0.310				

Crystals II

Temp., °K.	129.6	131.2	136.9	148.5	161.8	174.8	187.1	199.1
C_p per g.	0.321	0.324	0.329	0.341	0.354	0.366	0.380	0.391
Temp., °K.	210.7	222.0	230.5	233.6	236.2			
C_p per g.	0.409	0.422	0.431	0.435	0.439			

Liquid

Temp., °K.	253.2	258.5	275.3	275.7	281.6	293.9
C_p per g.	0.459	0.463	0.481	0.479	0.485	0.497

TABLE II

FUSION DATA[a]

No.	Substance	M. p., °K.	Heat of fusion (cal. per g.) 1st result	2nd result	Mean
1	*n*-Heptane	182.2	33.84	33.73	33.78
2	2-Methylhexane	154.0	21.17	21.16	21.16
4	3-Ethylpentane	154.3	22.47	22.66	22.56
5	2,2-Dimethylpentane	148.1	13.97	13.98	13.98
7	2,4-Dimethylpentane	152.5	16.00	15.94	15.97
8	3,3-Dimethylpentane	138.2	16.83	16.90	16.86
9	2,2,3-Trimethylbutane	247.7	5.18	5.32	5.25

[a] In the calculation of these fusion values, the marked rise in the specific heat of the solid as the melting point is approached was attributed to premelting and the heat absorbed in this region in excess of that obtained by extrapolation of the specific heat data at lower temperatures was added to the heat absorbed at the melting point.

The specific heats and the fusion data, expressed in terms of the 15° calorie[10] and with all weights reduced to a vacuum basis, appear in Tables I and II, respectively. For the sake of spatial economy in Table I, we have omitted the data for *n*-heptane and 2-methylhexane, as these have been given in an earlier paper.[8] As an illustration of the general character of

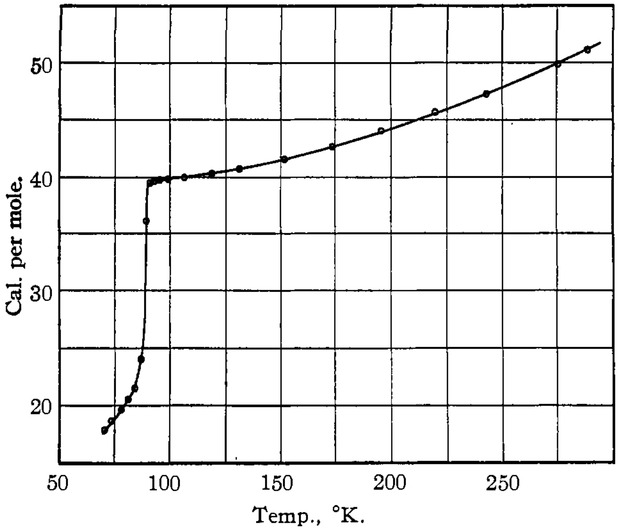

Fig. 1.—The molal heat capacity curve for 3-methylhexane.

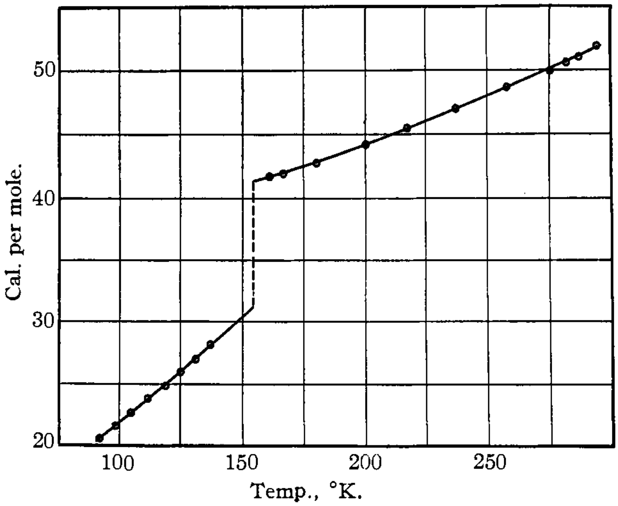

Fig. 2.—The molal heat capacity curve for 3-ethylpentane.

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[10] The factor 0.2390 has been used in converting the results from the joule to the 15° calorie.

the specific heat curves, we have plotted the molal heat capacities of 3-methylhexane and 3-ethylpentane in Figs. 1 and 2.

Two of the heptanes, 3-methylhexane and 2,3-dimethylpentane, failed to crystallize even when slowly cooled to 70°K. These compounds contain asymmetric carbon atoms. However, the liquids studied were optically inactive, being evidently mixtures of the dextro and levo forms in equal amounts. On progressive cooling, they became very viscous and finally solidified to clear glasses at about 100°K. Both substances showed the typical behavior which has been observed with other organic glasses, and the specific heat curves exhibit a 100% increase within a 10° interval.[11]

The last isomer, 2,2,3-trimethylbutane, evidently exists in at least two crystalline forms at low temperatures with a transition point at 121.0°K. The heat of transition was measured and found to be 5.67 cal. per g., a value which slightly exceeds the heat of fusion in magnitude. There was also a marked "hump" or maximum in the heat capacity curve for the low temperature form at about 105°K. The heat effect associated with this hump above the smooth specific heat curve was about 0.58 cal. per g. This particular compound showed no premelting and was apparently very pure.

Discussion

The Heat Capacity Curves.—Recently Andrews[12] has been quite successful in a theoretical analysis of the heat capacity curves for a number of crystalline organic compounds. He considers the values of C_p per mole for benzene, for instance, to be the sum of the energy increments due to intermolecular vibrations, to the various intramolecular vibrations and to the heat absorbed in the expansion of the crystal at constant pressure. The molecule, as a whole, possesses molecular vibrational energy, both translational and rotational, which may be approximately calculated with the aid of the Debye function. Within the benzene molecule the six CH groups possess vibrational energy for three degrees of freedom, which may be estimated by use of Einstein functions. Theoretically there also should be some energy associated with the vibrations of the individual hydrogen atoms, but the binding force of the carbon–hydrogen bond is so great that the magnitude of this vibrational energy is negligible below room temperature. From 0°K. to liquid air temperatures, practically all of the energy absorbed goes into the molecular vibrations. Above 100°K. the energy associated with the oscillations of the CH groups becomes increasingly important, amounting to almost one-half of the total heat capacity at the melting point; likewise, the rate of absorption of heat for the work of expansion, $C_p - C_v$, increases with the temperature, becoming about 10% of the total at 260°K.

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[11] Parks and Huffman, *J. Phys. Chem.*, 31, 1842 (1927).

[12] Andrews, *Chem. Reviews*, 5, 533 (1928).

In the course of our investigations upon these heptanes and other hydrocarbons, we have applied such theoretical considerations toward an explanation of the heat capacity curves for the crystalline, liquid and glassy states. While we intend to treat the subject from a more quantitative standpoint at a future date, it seems appropriate for us to present our views here in qualitative fashion. For this purpose we have constructed the curves in Fig. 3. The one bearing the label "crystals" represents the theoretical curve for a crystalline heptane, based upon these conceptions of Andrews. It may be considered as the resultant sum of a series of Debye functions (representing the vibrations of the molecule as a whole) and of a series of Einstein functions (representing the various types of vibrations of the several carbon groups in the molecule), there being added, of course, the correction for the $C_p - C_v$ difference.

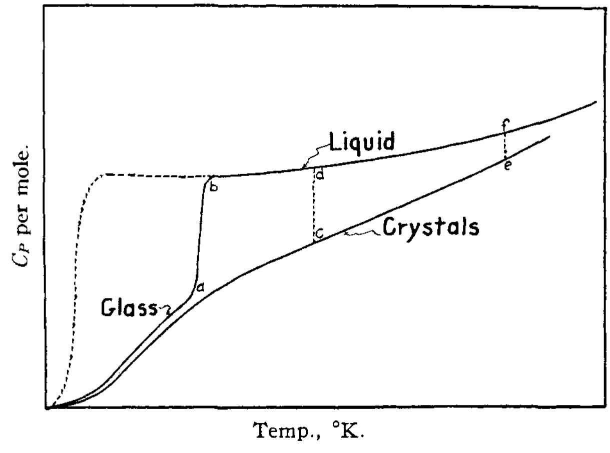

Fig. 3.

We believe that the same type of reasoning can be used to account for the heat capacity curve of a liquid heptane, at least up to room temperature. This amounts to adopting the picture that in a liquid, far below the boiling point, the motion of the molecular units is largely vibrational in character, although undoubtedly these vibrations are more or less anharmonic.[13] As a first approximation the heat capacity curve for such a liquid can be represented, as in the case of the crystalline phase, by the sum of a number of Debye and Einstein functions, in which, however, most of the vibrational frequencies are much lower than for the corresponding crystals, since the cohesive forces are weaker. Assuming for the instant

[13] Eucken, *Berl., Ber.*, 682 (1914), and Honda, *Phil. Mag.*, **45**, 189 (1923), have previously made a similar suggestion to account for the heat capacity of liquid mercury, etc. In this connection see also Eucken, Jette and LaMer, "Fundamentals of Physical Chemistry," McGraw-Hill Book Co., New York, **1925**, p. 159.

that the liquid state could be retained even to the lowest temperatures without "hardening" or vitrification, we would expect to obtain a curve somewhat like that labeled "liquid" in Fig. 3. With very low vibrational frequencies the Debye and Einstein functions would first give, at the lowest temperatures, rapidly increasing values which might reach a temporary maximum at, perhaps, 40°K. At still higher temperatures that part of the heat capacity due to the intermolecular vibrations would undoubtedly decrease as the vibrations become more anharmonic and tend to degenerate into translational and rotational motion. On the other hand, the heat capacities associated with some types of intramolecular oscillations certainly do not approach their limiting values below 500 or 600°K. Likewise, the $C_p - C_v$ difference must steadily increase with rising temperature, and this quantity is very considerable for such liquids (10 to 11 cal. per mole for the various heptanes at 293°K.). In view of these several factors the resultant molal heat capacity curve for a liquid heptane would probably flatten out in the neighborhood of liquid air temperatures and then increase but slowly in going up to room temperature.

Of course, the broken portion of the liquid curve is purely imaginary, as every known liquid on cooling either crystallizes or hardens to form a glass. In this connection the production of glasses from such typically non-polar liquids as 3-methylhexane and 2,3-dimethylpentane appears to us especially significant, since heretofore the only organic glasses studied were formed from more or less polar substances, containing carbon, hydrogen and oxygen. In the past the formation of a glass has sometimes been explained by assuming the production of highly associated groups, or even colloidal particles, on cooling the parent liquid. However, the extensive formation of associated groups in the two heptanes just mentioned seems rather improbable, and we believe that the true explanation of the vitrifaction of a liquid is to be found in a great increase, within a relatively small temperature interval, of the cohesive forces acting between the molecules.[14] As a result of this increase in cohesion, there should also be a marked increase in the vibrational frequencies for the oscillations of the molecular units and for the intramolecular oscillations of the individual carbon atoms along certain axes of motion; hence, in accordance with the Debye and Einstein functions, the resultant molal heat capacity might be expected to fall off rapidly within a small temperature interval. Experimentally this rapid change has been found for all organic glasses so far studied; it is indicated graphically by the line ab in Fig. 3. Since the glassy form of a substance

[14] This increase in the cohesive forces is probably the result of the volume shrinkage in the liquid, consequent to a decrease of the thermal motions with lowering of temperature. That such a change in cohesion takes place is evidenced by the tremendous increases in the viscosity of the parent liquid just above the "hardening point"—increases of a hundred-fold or more within ten degrees, Parks and Gilkey, *J. Phys. Chem.*, **33**, 1432 (1929).

ordinarily exhibits a heat capacity curve similar to but slightly above that for the crystalline form, it would seem that the cohesive forces, or internal pressures, in the two forms must be of about the same magnitude. In fact, we may picture the glassy and crystalline states as containing essentially the same units and as held together by essentially the same forces, the former merely lacking the regularity of arrangement of these units and forces found in the latter.

If the foregoing explanation for the formation of a glass be valid, we might expect that certain soft crystals, showing a large coefficient of thermal expansion and differing but slightly in energy content from the corresponding liquid form, might undergo a similar large change in internal cohesive forces and consequently a rapid fall in heat capacity within a brief temperature interval. In this connection it is interesting to note that Kelley[15] has studied such a substance in the form of the high-temperature modification of cyclohexanol and has observed a sharp drop in its heat capacity curve about 90° below the point of transition into the low-temperature modification.

Finally we might call attention to the significance of the lines cd and ef in the diagram. If the crystalline heptane be one which melts at a low temperature such as c, there should be a decided increase in heat capacity after fusion, the change being measured by the length of cd. On the other hand, if fusion takes place at a relatively high temperature e, the increase in specific heat should be small. These deductions are in agreement with the experimental data.

Entropies of the Heptanes.—Using our specific heat and fusion data in conjunction with the third law of thermodynamics, we have calculated the molal entropies at 298.1°K. for the seven heptanes which crystallized. In these calculations we have employed the extrapolation method of Kelley, Parks and Huffman[16] for estimating the entropy increases for the crystals (Col. 3 of Table III) from 0 to 90°K. The various entropy increments from 90 to 298°K., which appear in Cols. 4, 5 and 6 of the table, were obtained by the usual methods directly from the experimental data. The results for the total entropy in calories per degree appear under the heading "S_{298} experimental" in the seventh column; they are probably accurate to within 1%.

Although the third law of thermodynamics is not strictly applicable to non-crystalline substances, we have roughly estimated the entropies of 3-methylhexane and 2,3-dimethylpentane. In these instances we obtained graphically the entropy increment of the glass and liquid between 70 and 298.1°K. (Col. 6 of Table III). By comparison with the other heptanes we then estimated the increment between 0 and 70°K. and to this result we

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[15] Kelley, THIS JOURNAL, 51, 1402 (1929).

[16] Kelley, Parks and Huffman, *J. Phys. Chem.*, 33, 1802 (1929).

TABLE III

ENTROPIES OF THE HEPTANES PER MOLE

No.	Substance	Crystals 0–90°K.	Crystals Above 90°K.	Fusion	Liquid	S_{298} Experimental	S_{298} Predicted
1	*n*-Heptane	16.97	18.80	18.58	24.51	78.9	78.9
2	2-Methylhexane	16.76	13.92	13.75	30.86	75.3	74.4
3	3-Methylhexane	16.9[a]	. . .	. . .	57.15	74.0	74.4
4	3-Ethylpentane	16.46	13.47	14.63	30.09	74.6	74.4
5	2,2-Dimethylpentane	15.32	12.33	9.44	30.97	68.1	69.9
6	2,3-Dimethylpentane	16.6[a]	. . .	. . .	56.60	73.2	69.9
7	2,4-Dimethylpentane	15.75	13.14	10.48	30.37	69.7	69.9
8	3,3-Dimethylpentane	14.50	9.94	12.21	33.45	70.1	69.9
9	2,2,3-Trimethylbutane	14.0	39.79[b]	2.11	8.86	64.8	65.4

[a] This is the estimated value for the entropy of the glass at 70°K. [b] This value includes 4.67 E. U. for the transition at 121.0° and 0.55 E. U. for the entropy of the hump at 105°K.

added 4 E. U. for the entropy of the glass at the absolute zero. The whole procedure, while somewhat arbitrary, probably does not involve an error greater than 2.5 E. U. in the value below 70°, since Kelley[17] has recently shown that several organic glasses apparently have entropies between 2.6 and 4.6 E. U. at 0°K. The resulting values for S_{298} are probably accurate to within 3.0 E. U.

In a previous paper it was shown that the entropy of a liquid paraffin hydrocarbon could be calculated quite accurately by the equation, $S_{298} = 25.0 + 7.7n - 4.5r$, where n is the number of carbon atoms in the molecule and r represents the number of branches on the straight chain. In the present study we have again used this equation to obtain the values for "S_{298} predicted" in the last column of Table III. On the whole the predicted values are in very good agreement with the experimental results.

The Free Energies of the Heptanes.—We have also calculated the free energies of formation of these heptanes by means of the fundamental thermodynamic equation, $\Delta F = \Delta H - T\Delta S$.

The essential data are given in Table IV. The heats of combustion at constant pressure appear in Col. 3; they were recently determined by the U. S. Bureau of Standards[18] at 20° and have been recalculated to 25° for our present purpose. The various results are probably accurate to about 1000 cal. and indicate that the molal heats of combustion of these isomers are practically identical. The ΔH_{298} values were then calculated by use of 68,330 and 94,270 cal.[8] for the heats of combustion of hydrogen and graphitic carbon, respectively. Column 5 contains the entropy of formation of each compound, which is simply the difference between its S_{298} and the corresponding values for the entropies of the elements contained therein. For

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[17] Kelley, THIS JOURNAL, **51**, 785 (1929).

[18] Kharasch, *Bur. Standards J. Research,* **2**, 359 (1929).

this purpose the respective entropies of carbon and hydrogen were taken as 1.3 and 14.8 E. U. per gram atom.[8]

TABLE IV

THERMAL DATA AT 298.1°K.

(The 15° cal. is used throughout and all weights have been reduced to a vacuum basis)

No.	Substance	Heat of combustion at constant pressure	ΔH_{298} Cal.	ΔS_{298} E. U.	ΔF_{298} Cal.
1	*n*-Heptane	1,149,400	−57,100	−167.0	−7300
2	2-Methylhexane	1,148,400	−58,100	−170.6	−7200
3	3-Methylhexane	1,148,400	−58,100	−171.9	−6800
4	3-Ethylpentane	1,149,400	−57,100	−171.3	−6000
5	2,2-Dimethylpentane	1,147,400	−59,100	−177.8	−6100
6	2,3-Dimethylpentane	1,148,400	−58,100	−172.7	−6700
7	2,4-Dimethylpentane	1,148,400	−58,100	−176.2	−5600
8	3,3-Dimethylpentane	1,147,400	−59,100	−175.8	−6700
9	2,2,3-Trimethylbutane	1,147,400	−59,100	−181.1	−5100

The molal free energies appear in the last column of the table. As calculated from the individual heats of combustion the nine values lie very close together, the maximum difference being 2200 cal. between *n*-heptane and 2,2,3-trimethylbutane. However, if the heats of combustion of the isomers are assumed to be identical and 1,148,400 cal. per mole, the free energies of *n*-heptane and 3-ethylpentane will be lowered by 1000 cal., while the values for 2,2-dimethylpentane, 3,3-dimethylpentane and 2,2,3-trimethylbutane will be raised algebraically by an equal amount. The free energy difference between compounds 1 and 9 will then become 4200 cal.

In any event it is clear that increased branching among these isomers leads to a small increase in the free energy level. Taking the values as given in the table, we find that the effect of shortening the main chain by introducing side branches is to raise the free energy level by an average of 600 cal. per branch. This result, while small, agrees fairly well with the 900 cal. average for a similar change in the three octane isomers previously studied by the authors. In each instance it thus appears that the normal paraffin is thermodynamically the most stable in its group.

Before concluding we wish to thank Dr. Graham Edgar, Director of the Research Laboratory of the Ethyl Gasoline Corporation, for the loan of these hydrocarbon samples and for his encouragement in this research.

Summary

1. The heat capacities of the nine isomeric heptanes have been measured between liquid air temperature and that of the room.

2. A qualitative explanation of the typical heat capacity curves for the crystalline, glassy and liquid states has been suggested.

3. The entropies of the isomeric heptanes have been calculated from the heat capacity data. These results agree well with the values predicted by means of a simple, empirical equation.

4. The corresponding free energies have also been calculated. It appears that with increased branching in this group of heptane isomers the free energy level is raised by an average of 600 cal. for each side branch.

STANFORD UNIVERSITY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE RICE INSTITUTE]

ALPHA-TETRAHYDROFURFURYL CHLORIDE AND ALPHA-TETRAHYDROFURFURYL ETHERS

BY W. R. KIRNER

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In a recent paper from this Laboratory[1] the synthesis of α-furfuryl chloride and a few α-furfuryl ethers was described. The preparation of tetrahydrofurfuryl chloride has now been accomplished by a similar application of the Darzens reaction to tetrahydrofurfuryl alcohol. This alcohol is now available in quantity from the Miner Laboratories of Chicago. Furfuryl chloride was found to be a relatively unstable substance having a sharp odor and exhibiting lachrymatory properties and possessing an extremely reactive chlorine atom. Tetrahydrofurfuryl chloride, on the other hand, is a relatively stable substance with a mildly pleasant odor, exhibits no lachrymatory properties and has an extremely unreactive chlorine atom.

The synthesis of the tetrahydrofurfuryl ethers was first attempted by the method which was successfully used for the preparation of the furfuryl ethers, namely, treatment of the chloride with the desired alcohol in the presence of pulverized potassium hydroxide. Treatment of furfuryl chloride under these conditions gave high yields of ethers with the reaction occurring very rapidly. In the case of the tetrahydrofurfuryl chloride this method failed. It was found that the chlorine atom in tetrahydrofurfuryl chloride was very much less reactive than the chlorine atom in furfuryl chloride. Thus, in an attempt to prepare tetrahydrofurfuryl methyl ether, tetrahydrofurfuryl chloride was treated with pulverized potassium hydroxide and absolute methyl alcohol and refluxed for a considerable period of time at the boiling point of the alcohol. The reaction occurred extremely slowly and only to a slight extent. It is possible that this reaction might be used for the preparation of the higher ethers for then the reaction could be carried out at a much higher temperature than is possible when methyl alcohol is used. However, this proposed method of preparation of the tetrahydrofurfuryl ethers has the disadvantage that an unsaturated tetrahydrofuran derivative can be formed simultaneously due to the elimination of halogen acid by the basic reagent used, a reaction which was not possible in the case of furfuryl chloride. Thus

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[1] Kirner, THIS JOURNAL, 50, 1955 (1928).