[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Thermal Data on Organic Compounds. XVII. Some Heat Capacity, Entropy and Free Energy Data for Five Higher Olefins[1]

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The heats of hydrogenation of some representative olefins have recently been measured with remarkable accuracy by Kistiakowsky[2] and his collaborators; and in this connection they have kindly loaned us samples of these compounds for the determination of the heat capacities at low temperatures and thereby the calculation of the corresponding entropies and free energies of formation. In the present study we shall present data for *n*-heptene-1, 1,4-pentadiene, tetramethylethylene and the two diisobutylene isomers.

Materials

The preparation and properties of the *n*-heptene-1, 1,4-pentadiene and tetramethylethylene have already been described by Kistiakowsky, Ruhoff, Smith and Vaughan.[2] From the change in melting point during our fusion determinations we have estimated the purity of the heptene-1 to be at least 99.85 mole % and that of the pentadiene 99.90 mole %. While the purity of the tetramethylethylene was probably of a similar high order, a quantitative estimate in this case was prevented by the existence of a transition between its two crystalline forms at a temperature only 1.9° below the melting point, 198.5°K. Incidentally this proximity of the transition and melting points enabled us to perform an interesting qualitative experiment in which a narrow tube containing the olefin was immersed in an alcohol-bath cooled with solid carbon dioxide. By careful maintenance of a suitable temperature gradient in the bath it was then possible to obtain, coexistent in the tube, (1) a supernatant layer of liquid tetramethylethylene, (2) a middle layer of the crystals melting at 198.5° and (3) a bottom layer of the low temperature crystals.

The Harvard investigators also separated the two diisobutylene isomers from a large quantity of commercial material by a series of careful fractional distillations. As they will describe the properties of these compounds in detail in a subsequent paper, we shall simply say here that our fusion determinations indicated a purity of about 99.5 mole % for the low boiling isomer (supposedly 2,4,4-trimethylpentene-1) and about 98 mole % for the high boiling isomer (supposedly 2,4,4-trimethylpentene-2).

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.[3] In view of the accuracy of the various measurements involved, the error in the experimental values thereby obtained is probably less than 0.5% at all temperatures.

These heat capacity data, expressed in terms of the defined calorie[4] and with all weights reduced to a vacuum basis, appear in Tables I and II. The specific heat values are also represented

TABLE I

SPECIFIC HEATS IN CALORIES PER GRAM OF SUBSTANCE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
n-Heptene-1: Crystals					
80.4	0.1841	105.0	0.2215	128.9	0.2518
85.6	.1922	112.3	.2317	135.8	.2617
91.8	.2017	121.1	.2436	142.7	.2726
98.2	.2120				
Liquid					
151.1	0.4383	196.9	0.4485	242.5	0.4719
155.5	.4378	201.9	.4515	256.8	.4819
159.8	.4387	206.1	.4511	261.2	.4855
166.5	.4409	215.1	.4557	274.9	.4983
174.8	.4400	219.3	.4588	280.4	.5033
181.1	.4421	234.2	.4656	287.6	.5092
186.2	.4436	238.3	.4695	295.1	.5181
1,4-Pentadiene: Crystals					
82.4	0.2197	101.0	0.2553	110.7	0.2782
88.3	.2308	103.9	.2620	117.2	.2970
94.5	.2424				
Liquid					
125.4	0.4506	188.2	0.4471	255.6	0.4830
131.6	.4469	194.6	.4498	260.7	.4870
137.6	.4454	200.3	.4526	265.7	.4913
149.5	.4438	214.4	.4587	275.3	.5002
155.5	.4437	219.7	.4609	284.9	.5065
161.7	.4429	225.0	.4630	288.7	.5091
177.4	.4456	238.4	.4709	292.5	.5144
182.6	.4468	243.6	.4742		
Tetramethylethylene: Crystals					
82.6	0.2222	115.0	0.2824	156.3	0.3453
87.5	.2380	123.0	.2939	164.7	.3610
93.8	.2461	131.6	.3089	171.6	.3774
101.2	.2596	140.7	.3220	178.2	.3977
108.1	.2709	148.6	.3340	184.2	.4130

(1) This investigation represents a continuation of Project No. 29 of the American Petroleum Institute Research. Financial assistance in this work has been received from a fund donated jointly by the Standard Oil Company of California and the Shell Development Company.

(2) Kistiakowsky, Ruhoff, Smith and Vaughan, THIS JOURNAL, **57**, 876 (1935); **58**, 137, 146 (1936).

(3) Parks, *ibid.*, **47**, 338 (1925); also Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

(4) The factor 1.0004/4.185 has been used in converting the international joule to the calorie (defined unit).

TABLE I (*Concluded*)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
		Liquid			
202.4	0.4395	232.3	0.4522	277.0	0.4829
209.8	.4412	241.9	.4570	282.8	.4877
214.6	.4430	247.3	.4605	291.2	.4955
226.8	.4492	263.9	.4722	295.5	.4991
Diisobutylene (low boiling isomer): Crystals					
80.9	0.1674	111.8	0.2302	148.1	0.2804
86.5	.1765	119.8	.2395	154.2	.2891
92.6	.1884	127.1	.2502	160.3	.3026
98.4	.2091	134.6	.2608	165.8	.3242
105.2	.2220	141.2	.2700		
		Liquid			
178.4	0.4043	216.4	0.4288	265.2	0.4691
187.1	.4102	222.1	.4338	275.2	.4783
192.6	.4137	235.7	.4431	280.9	.4844
200.8	.4185	253.3	.4575	288.3	.4919
206.1	.4227	259.5	.4637	296.0	.5013
Diisobutylene (high boiling isomer): Crystals					
81.1	0.1761	104.3	0.2295	131.0	0.2789
86.5	.1853	111.3	.2409	137.6	.2986
92.3	.1962	116.8	.2487	143.8	.3256
98.1	.2095	123.9	.2604		
		Liquid			
170.0	0.4085	216.7	0.4411	260.8	0.4744
175.0	.4121	222.1	.4445	276.3	.4898
190.8	.4233	236.7	.4551	282.1	.4952
200.3	.4293	241.9	.4585	289.6	.5021
205.6	.4335	255.6	.4696	298.6	.5116

TABLE II

FUSION DATA

Substance	M. p., °K.	Heat of fusion (cal. per g.) I	II	Mean
n-Heptene-1	153.4	30.77	30.86	30.82
1,4-Pentadiene	124.3	21.55	21.54	21.55
Tetramethylethylene	198.5	15.50	15.53	15.51
Diisobutylene, l. b.	178.9	18.68	18.67	18.67
Diisobutylene, h. b.	166	14.44	14.49	14.47

graphically in Figs. 1 and 2. It is interesting to note that the curve for liquid pentadiene shows a marked minimum similar to that found previously with butene-1, *cis*-butene-2 and propylene.[5] Another noteworthy point is that the specific heat curves for both diisobutylene isomers exhibit some sort of minor transition with a slight but appreciable rise at about 101°K. The heat effect associated with this transition seemed almost negligible—1.85 cal. per mole in the case of the low boiling isomer. A sample of diisobutylene, which was in reality a mixture of the isomers with the low boiling predominating, has been studied previously by Parks and Huffman.[6] In the present case our values for the low boiling compound agree for the most part to within 1% with these earlier, less reliable data.

In the calculation of the fusion values, the somewhat more rapid rise in the specific heat of the crystals 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. In the case of tetramethylethylene the transition point in the crystals at 196.6°K. was so close to the melting point that entirely independent determinations of the heat of transition and heat of fusion were impractical. Accordingly the sum of these heat effects was measured and from the relative time intervals for these two steps the fusion results in Table II were then derived. The corresponding values obtained for the heat of transition of tetramethylethylene were: I, 13.00 cal.; II, 13.01 cal.; mean, 13.00 cal. per g.

Entropy Data

Using the heat capacity data contained in the preceding section in conjunction with the third law of thermodynamics, we have calculated the entropies at 298.1°K. for these five substances. The detailed entropy values are given in Table III. In these calculations we have employed the extrapolation method of Kelley, Parks and Huffman[7] for estimating the entropy increases for the crystals (Column 2) from 0 to 80°K. The various increments from 80 to 298.1°K., which appear in the next three columns, were obtained by the usual methods directly from the experimental data. The results for the total entropy in calories per degree per mole are then given in the sixth column under the heading "S°_{298} olefin"; they are probably reliable to within 1.0 e. u. in an absolute sense and to 0.5 e. u. for comparative purposes.

In the seventh column of Table III we have tabulated entropy values,[6,8] derived previously in this Laboratory, for *n*-heptane, *n*-pentane, and 2,2,4-trimethylpentane, the paraffin hydrocarbons produced on the hydrogenation of four of these olefins. The last column then shows the

(5) Todd and Parks, THIS JOURNAL, **58**, 134 (1936).

(6) Parks and Huffman, *ibid.*, **52**, 4381 (1930).

(7) Kelley, Parks and Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).

(8) Parks, Huffman and Thomas, THIS JOURNAL, **52**, 1032 (1930). Corrections made since this earlier publication have altered the entropy values for *n*-heptane and 2,2,4-trimethylpentane by −0.1 to +0.2 e. u., respectively.

TABLE III

ENTROPIES OF THE LIQUID OLEFINS PER MOLE

Substance	Crystals 0–80°K.	Crystals Above 80°K.	Fusion	Liquid	S°_{298} olefin	S°_{298} paraffin	ΔS paraffin–olefin
n-Heptene-1	14.00	14.70	19.71	30.18	78.6	78.8	0.2
1,4-Pentadiene	11.26	7.65	11.80	27.44	58.2	62.0	1.9 × 2
Tetramethylethylene	13.97	23.24	12.13[a]	15.80	65.1	..	.....
Diisobutylene, low boiling	14.28	21.79	11.70	25.44	73.2	75.4	2.2
Diisobutylene, high boiling	14.94	20.10	9.77	29.68	74.5	75.4	0.9

[a] This value includes the entropy of transition (5.56 e. u.) between the two crystalline forms at 196.6 °K.

differences between the molal entropies of these corresponding paraffins and olefins or, in other words, the entropy decreases for the formation of the olefin double bond. Undoubtedly this effect depends considerably upon the position of the double bond in the molecule and upon symmetry considerations.[9] In the present case the average entropy decrease per double bond is 1.4 e. u. and this figure, while it cannot be considered very significant, is probably preferable to the decrease of 2.7 e. u. suggested previously by Parks and Huffman[6] from data pertaining mainly to crystalline unsaturated acids and various cyclic compounds.

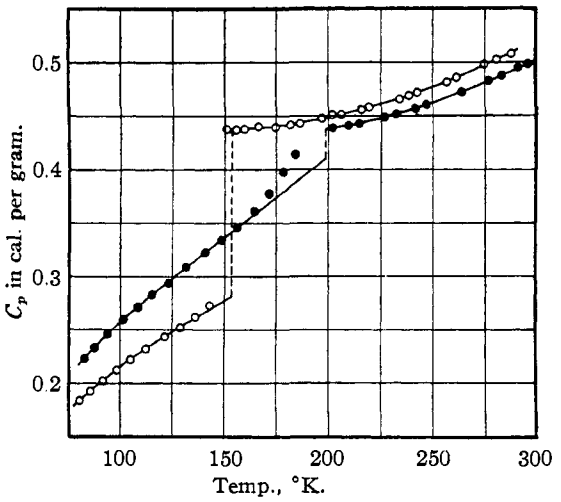

Fig. 1.—The specific heat curves for *n*-heptene-1 (circles) and tetramethylethylene (heavy dots).

Free Energy Data

We have also calculated the free energies of formation of four of these olefins in the liquid state by means of the fundamental equation, $\Delta F = \Delta H - T\Delta S$. The essential thermal data are given in Table IV.

The values for the ΔH°_{298} of formation of these compounds were obtained by a combination of the ΔH°_{298} values for the corresponding or parent

(9) In this connection see Kassel, *J. Chem. Phys.*, **4**, 435 (1936).

TABLE IV

THERMAL DATA AT 298.1°K. FOR THE OLEFINS

In calories per mole with all weights reduced to a vacuum basis.

Substance	ΔH°_{298}, cal.	ΔS°_{298}, e. u.	ΔF°_{298}, cal.
n-Heptene-1 (1)	−25,520	−149.5	19,050
1,4-Pentadiene (1)	18,060	− 73.5	39,970
Diisobutylene l. b. (1)	−36,360	−187.5	19,530
Diisobutylene h. b. (1)	−35,250	−186.2	20,260

paraffins with the heats of hydrogenation of Kistiakowsky and collaborators.[10] The heats of formation of these particular liquid paraffins have already been calculated by Parks[11] with the aid of the highly accurate combustion data obtained in recent years by Rossini and his collaborators

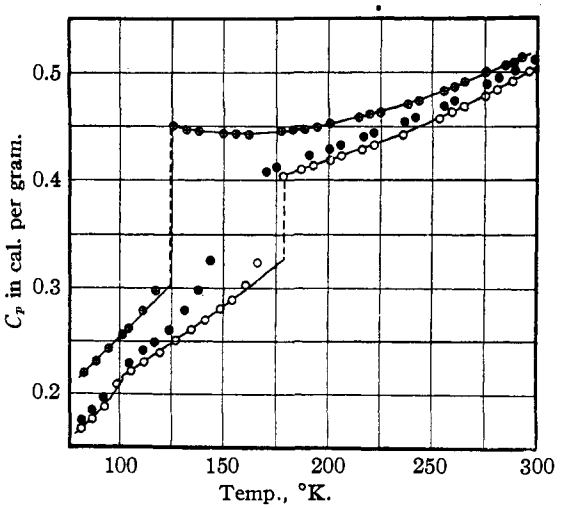

Fig. 2.—The specific heat curves for 1,4-pentadiene (crossed circles) and the low boiling diisobutylene (plain circles). The specific heat values for the high boiling diisobutylene (m. p. 166°) are represented by the heavy dots without a curve.

at the U. S. Bureau of Standards. To these values for the parent paraffins we have then added

(10) The heats of hydrogenation for the diisobutylene isomers have not been published yet. A private communication from the Harvard laboratory gives these as 27,236 cal. per mole for the low-boiling and 28,352 cal. per mole for the high-boiling isomer in the gas phase at 355°K. In the latter case there is considerable uncertainty as to the effect of the impurities on this hydrogenation value. The data for the three other olefins are available in ref. 2.

(11) Parks, *Chem. Rev.*, **18**, 325 (1935).

Kistiakowsky's hydrogenation results, reduced by a uniform 250 cal. (500 cal. in the case of pentadiene) to convert the data from 355 to 298° K. In this connection we have assumed that these heats of hydrogenation, although determined for the gas-phase reaction, can be applied without alteration to the process involving the hydrocarbons in the pure liquid state.

The ΔS°_{298} values represent simply the differences between the S°_{298} for each olefin and the corresponding values for the entropies of the elements contained therein. For this purpose we have used 15.615 e. u.[12] for the entropy of $^1/_2H_2$ and 1.36 e. u.[13] for C (β-graphite).

The molal free energies appear in the last column of the table. The errors in these values are probably within 800 cal. for *n*-heptene-1 and 1,4-pentadiene, within 1500 cal. for low boiling diisobutylene and within 2000 cal. for high boiling diisobutylene.

Comparing the free energy of heptene-1 with that calculated by Parks[11,8] for *n*-heptane, we find ΔF°_{298} = 20,620 cal. for the dehydrogenation process

$$n\text{-heptane} \longrightarrow n\text{-heptene-1} + H_2$$

Likewise in the case of 1,4-pentadiene and *n*-pentane the difference is 2 times 21,400 cal. Previously Parks[11] has estimated 21,040 cal. and 21,360 cal., respectively, for the propylene–propane and butene-1–*n*-butane differences. Hence, the free energy change in the formation of a normal α olefin by dehydrogenation of a paraffin is apparently around 21,000 cal. irrespective of the length of the paraffin chain.

The addition of more methyl or other radicals to the carbon atoms adjacent to the double bond, however, leads to definitely lower values for this ΔF°_{298} of dehydrogenation. Thus with branched molecules, such as isobutene and 2,4,4-trimethylpentene-1, the free energy difference drops noticeably, being 18,180 cal. in the latter case. The same trend appears also when the double bond is shifted from the α- to the β-position, as shown by Todd and Parks[5] in the cases of *cis*- and *trans*–butene-2. Next with the trimethylethylene–methylbutane combination, involving three methyl substituents on the ethylene group, we calculate ΔF°_{298} = 17,360 cal., using the hydrogenation data of the Harvard laboratory[2] in conjunction with the proper experimental entropy values.[14] Of course, the end-point in this series is the tetramethylethylene–tetramethylethane combination for which an exact calculation of the ΔF°_{298} of dehydrogenation is at present impossible in the absence of an experimental entropy value for the paraffin compound. However, for the dehydrogenation in this case ΔH°_{298} is only 26,380 cal. and, if we assume equal entropies for the olefin and parent paraffin (an assumption that cannot involve us in any serious error), ΔF°_{298} is estimated as approximately 17,100 cal.—a figure about 4000 cal. lower than with the dehydrogenations that yield the normal α olefins. In other words, with additional spatial protection to the ethylene group the olefins become progressively less unstable with reference to the parent paraffin hydrocarbons.

Summary

1. The specific heats of *n*-heptene-1, 1,4-pentadiene, tetramethylethylene and the two diisobutylene isomers have been measured between 80 and 298°K. The corresponding heats of fusion have also been determined.

2. The entropies of these five olefins in the liquid state at 298.1°K. have been calculated from the foregoing heat capacity data.

3. The corresponding free energies (except in the case of tetramethylethylene) have also been calculated. Among the α olefins the free energy difference between an olefin and the corresponding paraffin is uniformly about 21,000 cal. As the number of radicals attached to the carbon atoms of the ethylene linkage increases this free energy of dehydrogenation falls off progressively to about 17,100 cal. as a limit.

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(12) Giauque, THIS JOURNAL, **52**, 4825 (1930).

(13) Jacobs and Parks, *ibid.*, **56**, 1513 (1934).

(14) It should be noted here that S°_{298} for liquid 2-methylbutane is 59.5 e. u. instead of 60.8 e. u., as erroneously reported in References 6 and 8.