[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Thermal Data on Organic Compounds. XV. Some Heat Capacity, Entropy and Free Energy Data for the Isomeric Butenes[1]

BY SAMUEL S. TODD AND GEORGE S. PARKS

In this investigation the heat capacities of the four isomeric butenes have been measured between liquid air temperatures and their respective boiling points. The results, combined with other suitable data, suffice for a calculation of the molal entropies and the free energies of formation of the compounds at 298.1°K. These latter values show that the thermodynamic stability varies considerably with the configuration of the molecule.

Materials

The two forms of butene 2 were prepared under the direction of Professor G. B. Kistiakowsky in the chemical laboratory of Harvard University by Dr. J. R. Ruhoff, assisted by Mr. Edwin E. Roper, Mr. W. R. Smith and Dr. G. F. Wright. Full preparative details have already been published by Kistiakowsky[2] and his collaborators. From the fusion determinations in our own laboratory we have estimated that the purity of the samples sent to us was better than 99.9 mole %. Throughout this paper the low boiling isomer will be referred to as the *trans* form, and the high boiling isomer as the *cis* form.

The butene-1 sample was also prepared by the Harvard investigators and loaned to us for the present measurements. While presumably of the same purity as the butene-2 isomers, we were unable to crystallize this compound, although we kept a 20-g. portion at 78°K. for several days.

The isobutene sample was kindly prepared for us by the research laboratory of the Shell Development Company. Dehydration of very pure tertiary butyl alcohol and fractionation of the resulting product yielded a material which we estimated by freezing point measurements to be about 99.9 mole % pure.

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

TABLE I

SPECIFIC HEATS IN CALORIES PER GRAM OF SUBSTANCE

T., °K.	C_p	T., °K.	C_p	T., °K.	C_p
		Butene-1: Liquid			
81.3	0.4736	142.5	0.4505	202.0	0.4706
86.8	.4684	149.0	.4514	217.2	.4788
92.8	.4634	155.4	.4522	223.2	.4827
96.7	.4607	163.3	.4539	229.0	.4864
102.2	.4575	175.7	.4572	234.8	.4923
108.6	.4558	181.9	.4590	240.6	.4959
118.0	.4521	188.0	.4621	247.8	.5016
134.5	.4505	195.8	.4670	253.4	.5076
		cis-Butene-2: Crystals			
93.6	0.2613	107.0	0.2887	116.5	0.3064
98.7	.2722	110.2	.2930	122.2	.3168
100.5	.2747	113.8	.3011	127.6	.3362
		Liquid			
138.2	0.4803	180.0	0.4704	231.0	0.4828
145.0	.4766	192.2	.4717	243.5	.4895
152.8	.4737	198.2	.4731	249.6	.4932
161.8	.4716	211.7	.4756	255.3	.4970
167.8	.4711	218.2	.4782	261.0	.5021
174.0	.4711	224.6	.4800	266.6	.5064
		trans-Butene-2: Crystals			
93.6	0.2462	125.9	0.3225	142.1	0.3691
99.1	.2592	134.2	.3433	149.5	.3978
105.7	.2741				
		Liquid			
176.0	0.4703	215.7	0.4883	253.6	0.5141
182.5	.4722	221.8	.4920	259.6	.5199
		Isobutene: Crystals			
93.3	0.2498	105.5	0.2749	118.9	0.3056
98.8	.2614	112.3	.2898	125.1	.3261
		Liquid			
139.2	0.4547	172.9	0.4650	227.9	0.4970
145.2	.4564	179.8	.4681	237.0	.5037
152.0	.4579	186.5	.4715	242.7	.5089
159.1	.4600	210.2	.4860	248.0	.5133
166.1	.4621	216.2	.4896	253.1	.5173

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[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).

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

TABLE II

FUSION DATA

Substance	M. p., °K.	Heat of fusion (cal. per g.) I	II	Mean
cis-Butene-2	133.8	31.17	31.17	31.17
trans-Butene-2	167.3	41.91[a]	42.01	42.00
Isobutene	132.4	25.22	...	25.22

[a] This particular fusion determination was made with a smaller sample than usual and there is reason for believing that it is a few tenths of a per cent. low.

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 graphically in Figs. 1 and 2. It is interesting to note that the curves for liquid butene-1 and *cis*-butene-2 show distinct minima at 138 and 178°K., respectively. Perhaps the higher specific heats at temperatures below these points are to be attributed to some "association" in the liquid phase as a result of the small electric moments arising from the molecular structures. Such dipole interaction would naturally hinder the crystallization process and might account for the failure of the butene-1 to crystallize, in spite of the apparent purity of the sample. Huffman, Parks and Barmore[5] have noted a similar minimum in their earlier measurements on liquid propylene.

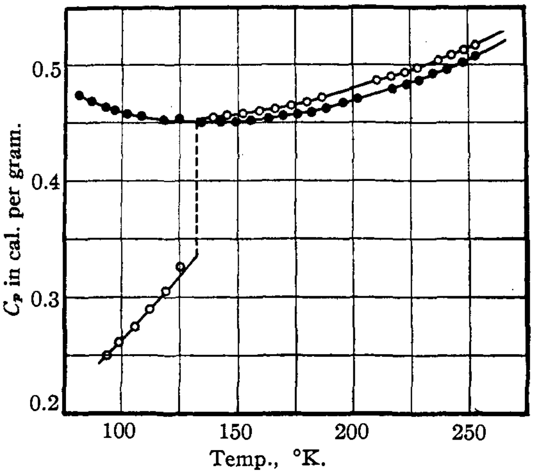

Fig. 1.—The specific heat curves for butene-1 (heavy dots) and isobutene (circles).

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.

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 the butene-2 isomers and isobutene in the gaseous state at 1 atm. The detailed data are given in Table III. In these calculations we have employed the extrapolation method of Kelley, Parks and Huffman[6] for estimating the entropy increases for the crystals (line 1 in the table) from 0 to 90°K. The various entropy increments from 90° to the respective boiling points[2] (276.8° for *cis*-butene-2, 274.1° for *trans*-butene-2 and 266.0° for isobutene) were obtained by the usual methods directly from the experimental data and appear in the next three lines of the table. The values for the entropy of vaporization are estimates which we have made in the light of the published work of Kistiakowsky[2] and collaborators, and of Coffin and Maass[7] and some preliminary data of Mr. E. E. Roper;[8] they are probably good to ±0.2 e. u. The entropy increases for the gases to 298.1°K. were made by assumption of the same heat capacity equation, $C_p = 19.9 + 0.027\ (T - 273.1)$, for all three butenes. While it is only an approximation which we have derived from the studies of Lewis and McAdams[9] and Eucken and

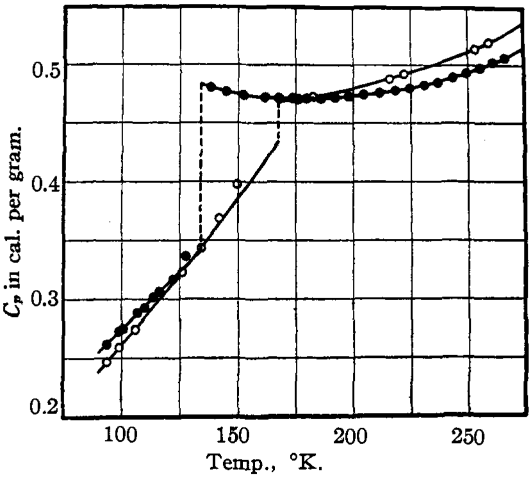

Fig. 2.—The specific heat curves for *cis*-butene-2 (heavy dots) and *trans*-butene-2 (circles).

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

(5) Huffman, Parks and Barmore, THIS JOURNAL, **53**, 3876 (1931).

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

(7) Coffin and Maass, THIS JOURNAL, **50**, 1427 (1928).

(8) E. E. Roper, private communication to the authors.

(9) Lewis and McAdams, *Chem. Met. Eng.*, **36**, 336 (1929).

Parts,[10] this equation cannot involve us in any serious error over such short temperature intervals. The results for the total entropy in calories per degree per mole are then given in the last line of the table; they are probably reliable to within 1.0 e. u. in an absolute sense and to 0.5 e. u. for comparative purposes.

TABLE III

MOLAL ENTROPIES OF THREE ISOMERIC BUTENES

Compound	*Cis*-2	*Trans*-2	Isobutene
Crystals (0 to 90°)	11.70	10.23	10.81
Crystals (above 90°)	6.55	11.18	6.17
Fusion	13.06	14.07	10.68
Liquid	19.57	13.61	18.72
Vaporization	20.63	20.41	20.33
Gas (to 298.1°)	1.50	1.70	2.29
S°_{298}	73.0	71.2	69.0

Our failure to crystallize the butene-1 sample precludes a direct calculation of the entropy of this olefin from the heat capacity data. However, with the aid of the experimental values obtained for the closely related butene-2 isomers and the marked entropy regularities brought to light by Parks and Huffman[11] in their previous studies on organic compounds, we have been able to estimate 72.5 (±1.3) e. u. per mole for butene-1. This value will amply suffice for our purposes in the following section.

Free Energy Values for the Isomeric Butenes

We have also calculated the free energies of formation of these four butenes in the gaseous 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 Rossini's recent combustion data[12] with the heats of hydrogenation of Kistiakowsky and collaborators.[2] Rossini found −30,570 cal. and −32,200 cal. for the ΔH°_{298} of formation of *n*-butane and isobutane, respectively, from hydrogen and β-graphite. To these values for the parent paraffins we have then added Kistiakowsky's hydrogenation results for the four butenes, reduced by a uniform 250 cal. to convert the data from 355 to 298°K., and thus have obtained the quantities given in the second column of the table. In view of the accuracy of the calorimetric measurements on which they depend, these ΔH°_{298} values are probably reliable to within 200 cal. for comparative purposes.

TABLE IV

THERMAL DATA AT 298.1°K. FOR THE BUTENES

The defined calorie is used throughout and all weights have been reduced to a vacuum basis

Substance	ΔH°_{298}', cal.	ΔS°_{298}', e. u.	ΔF°_{298}', cal.
Butene-1 (g)	− 480	−57.9	16,780
cis-Butene-2 (g)	−2250	−57.4	14,860
trans-Butene-2 (g)	−3200	−59.2	14,450
Isobutene (g)	−4060	−61.4	14,240

The ΔS°_{298} values represent simply the differences between the S°_{298} for each butene and the corresponding values for the entropies of the elements contained therein. For this purpose we have used 15.615 e. u.[13] for the entropy of $^1/_2H_2$ and 1.36 e. u.[14] for C (β-graphite).

The molal free energies appear in the last column of the table. The errors in these values are probably within 500 cal. for the last three of these olefins and within 600 cal. for the butene-1. However, for comparative purposes the data are without doubt considerably more reliable than such figures might indicate. Thus the free energy difference of 410 cal. between the butene-2 isomers can hardly be in error by more than 250 cal. Hence, the data show clearly that the order of increasing thermodynamic stability among the normal butenes is butene-1, *cis*-butene-2 and *trans*-butene-2, and that probably the branched isobutene is even slightly more stable than the last of these. The results also provide a thermodynamic explanation for the known tendency of α-olefins to rearrange or for the double bond to shift its position to a more central position in the molecule.[15]

The free energies of the three normal butenes may also be estimated from Frey and Huppke's[16] study of the equilibrium dehydrogenation of *n*-butane at 623, 673 and 723°K. We have recently recalculated their free energy equations, using $\Delta C_p = 4.0$ cal. for the dehydrogenation reactions and Kistiakowsky's accurate heats of reaction. Relying mainly on the values of the equilibrium constants at 673°, the intermediate temperature

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[10] Eucken and Parts, *Z. physik. Chem.*, **20B**, 184 (1933).

[11] Parks and Huffman, "The Free Energies of Some Organic Compounds," Chemical Catalog Co., New York City, 1932, p. 209.

[12] Rossini, *Bur. Standards J. Research*, **13**, 21 (1934); **15**, 357 (1935); *J. Chem. Phys.*, **3**, 438 (1935).

[13] Giauque, THIS JOURNAL, **52**, 4825 (1930).

[14] Jacobs and Parks, *ibid.*, **56**, 1513 (1934).

[15] Norris and Reuter, *ibid.*, **49**, 2624 (1927); see also Brooks, "The Non-Benzenoid Hydrocarbons," Chemical Catalog Co., New York, N. Y., 1922, p. 178.

[16] Frey and Huppke, *Ind. Eng. Chem.*, **25**, 54 (1933).

in the measurements, we have found 20,900, 19,620 and 18,850 cal., respectively, for the ΔF°_{298} in the process of dehydrogenating *n*-butane to yield butene-1, *cis*-butene-2 and *trans*-butene-2. The ΔF°_{298} of formation of *n*-butane[11] (p. 64) recalculated with Rossini's new combustion value is −4580 (±300) cal. We thus obtain 16,320, 15,040 and 14,270 cal. for the ΔF°_{298} of formation of butene-1, *cis*-butene-2 and *trans*-butene-2, respectively, from the elements. These values, though not as reliable, are in good agreement with those just found in Table IV and serve to place the normal butenes in the same order of thermodynamic stability.

Before concluding, we wish to take this opportunity to thank the investigators in the chemical laboratory of Harvard University for the remarkably pure butene samples, without which this study would have been impossible.

Summary

1. The heat capacities of the four isomeric butenes have been measured between liquid air temperatures and their respective boiling points.

2. The entropies of *cis*-butene-2, *trans*-butene-2 and isobutene at 298.1°K. have been calculated from these heat capacities in conjunction with other data. An estimate has been made for the entropy of butene-1.

3. The free energies of formation of these four butenes have also been calculated. The order of increasing thermodynamic stability is apparently: butene-1, *cis*-butene-2, *trans*-butene-2, isobutene.

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RECEIVED NOVEMBER 2, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Heats of Organic Reactions
III. Hydrogenation of Some Higher Olefins

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The first and second communications[1] of this series have dealt with a calorimeter for the determination of the heats of hydrogenation of organic compounds in the vapor phase and with the results thus far obtained on ethylene and some of its simpler homologs. The present paper is concerned with further measurements on ethylene homologs of higher molecular weight. While this line of inquiry is not yet completed, some regularities of rather general applicability can be noted and will be discussed after the presentation of the results. However, before proceeding to this main subject, it is desirable to devote some space to a renewed consideration of the accuracy of the method developed; this is being reviewed because, as has been recently pointed out,[2] there exists a considerable discrepancy between the observed position of the thermal equilibrium in the ethane–ethylene–hydrogen system and that which is calculated using the new value for the heat of hydrogenation and computing entropies and heat capacities statistically. This conclusion has also been reached independently by Topley and Teller,[3] who have made a more exhaustive consideration of all possible sources of error in the calculations; these authors conclude in effect that the true heat of hydrogenation is lower at least by 900 and more likely by some 1500 calories than that given in the first paper of this series. Smith and Vaughan, on the other hand, are inclined to attribute the discrepancy to an incorrect calculation of the rotational entropy of ethane.

On the Reliability of the Method

The situation described above clearly indicates the desirability of further search for possible experimental errors. Besides those which have been adequately dealt with in the first and second publications, an error could result if the compounds used were irreversibly adsorbed on the catalyst. If this hypothetical exothermic process, probably accompanied by partial hydrogenation and polymerization, were to take place at a steady rate during all measurements on a given compound, self-consistent results would be obtained, but they would be too high. To test this rather un-

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[1] (a) Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, THIS JOURNAL, **57**, 65 (1935), hereinafter called I; (b) Kistiakowsky, Ruhoff, Smith and Vaughan, *ibid.*, **57**, 876 (1935), hereinafter called II.

[2] Smith and Vaughan, *J. Chem. Phys.*, **3**, 341 (1935).

[3] Topley and Teller, *J. Chem. Soc.*, 876 (1935).