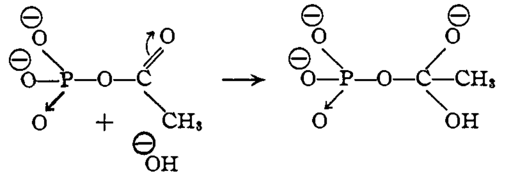
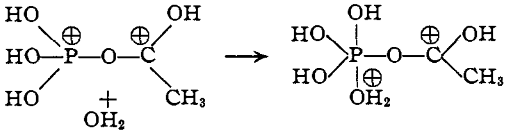
proceeds by different mechanisms depending on the pH of the solution.[14a,b]

A somewhat similar behavior has been observed with some lactones[15] and in the hydrolysis of trimethyl orthophosphate.[16]

It is tentatively suggested that the mechanism of hydrolysis of acetyl dihydrogen phosphate can be expressed in terms similar to those which have been proposed for ester hydrolysis. In alkaline solution, the attack is by the nucleophilic hydroxyl ion on the ionized molecule. In view of the negatively charged oxygen atoms surrounding the phosphorus atom the carbon atom will be more readily attacked, and the initial stage of alkaline hydrolysis may be pictured as



Under acid conditions, again due to the influence of the hydroxyl groups (now un-ionized), the phosphorus atom will have a greater capacity for sharing electrons, and the primary reaction will be of the type indicated below.



It seems likely that a similar pH effect would be observed with the mixed anhydrides of carboxylic acids, and there is already some evidence for this. Mixed anhydrides are known to react in different ways, depending on the reactant and the conditions. Thus, for example, the mixed anhydride of acetic and formic acids reacts with alcohols to form formic esters, but with phenols, the main products are the phenol esters of acetic acid.[17] It has also been shown that when this anhydride reacts with nitro-alcohols, etc., at 50–60°, formic esters are obtained. At higher temperatures, or in the presence of sulfuric acid, the acetates are produced.[18] It is possible that acetyl dihydrogen phosphate, under suitable conditions, could be used as a phosphorylating agent. No evidence has yet been obtained for non-enzymatic phosphorylations with this anhydride.[5]

Acknowledgment.—The author wishes to express his gratitude to Dr. D. Rittenberg for constant encouragement and advice during the course of the work described in this, and the earlier paper[5]; and to Mr. I. Sucher for the isotope analyses.

Summary

1. On hydrolysis under alkaline conditions acetyl dihydrogen phosphate and acetyl dibenzyl phosphate are split between the carbon and oxygen bond. Under acid conditions the phosphorus–oxygen bond is ruptured.

2. In the enzymic hydrolysis with acetyl phosphatase, the phosphorus–oxygen bond is split.

3. The probable primary reactions are discussed.

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(14) (a) E. H. Ingold and C. K. Ingold, *J. Chem. Soc.*, 756 (1932); (b) S. C. Datta, J. N. E. Day and C. K. Ingold, *ibid.*, 838 (1939).

(15) A. R. Olson and J. L. Hyde, THIS JOURNAL, **63**, 2459 (1941).

(16) E. Blumenthal and J. B. M. Herbert, *Trans. Faraday Soc.*, **41**, 611 (1945).

(17) A. Béhal, *Ann. chim. phys.*, [7] **20**, 419, 426 (1900).

(18) C. D. Hurd, S. S. Drake and O. Fancher, THIS JOURNAL, **68**, 789 (1946).

(19) Original manuscript received January 13, 1948.

[CONTRIBUTION NO. 16 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES, BARTLESVILLE, OKLA.]

Thermodynamic Properties of Three Isomeric Pentenes[1]

BY D. W. SCOTT, GUY WADDINGTON, J. C. SMITH[2] AND H. M. HUFFMAN

In continuation of the program of the Bureau of Mines for studying the thermodynamic properties of hydrocarbons and related compounds, vapor heat capacities, heats of vaporization, and vapor pressures have been measured for three of the isomeric pentenes, namely, 1-pentene, 2-methyl-1-butene and 2-methyl-2-butene. The entropies of vaporization derived from these measurements, when added to the entropies of the liquid substances found in a previous investigation in this laboratory,[3] have yielded values for the entropies of the three compounds in the vapor state. The calorimetric data for 2-methyl-2-butene have been correlated and extended to other thermodynamic functions and to higher temperatures by means of statistical mechanical calculations based on spectroscopic and molecular structure information.

Methods and Results

Vapor Heat Capacities and Heats of Vaporization.—Measurements of vapor heat capacities and heats of vaporization were made with the flow calorimeter and cycling vaporizer described

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(1) Presented in part before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the Chicago meeting, April, 1948. Article not copyrighted.

(2) Present address, Army, Chemical Center, Edgewood, Md.

(3) Todd, Oliver and Huffman, THIS JOURNAL, **69**, 1519 (1947).

in detail in previous publications from this Laboratory.[4,5] The purity of the pentenes[6] used for these measurements was determined from the analysis of time–temperature freezing point curves,[7] and the values obtained were: 1-pentene, 99.2 mole percent; 2-methyl-1-butene, 99.3 mole percent; and 2-methyl-2-butene, 99.7 mole percent. These purity values are subject to the usual assumptions of liquid-soluble solid-insoluble impurities and of ideal behavior.

The heat capacities of the vapors were measured at two or more pressures for each of five different temperatures between the normal boiling points of the compounds and 230°. The results are tabulated in Table I. Values of $C_p°$, the heat capacity in the ideal gas state, were obtained by linear extrapolation to zero pressure of plots of heat capacity *vs.* pressure. Because of the low boiling points of these compounds, it was not feasible to make measurements at pressures as low as those used with the higher boiling compounds previously studied in the same apparatus.[4,5,8] The extrapolations to zero pressure are therefore longer and introduce somewhat more uncertainty into the values obtained for $C_p°$. However, it is believed that the values of $C_p°$ given in Table I are accurate to 0.3%. Over the temperature ranges covered by the measurements, $C_p°$ as a function of temperature may be represented by empirical equations

1-Pentene: (±0.1%, 311–471°K.)

$$C_p° = 2.38 + 8.597 \times 10^{-2}T - 2.324 \times 10^{-5}T^2 \quad (1)$$

2-Methyl-1-butene: (±0.1%, 321–502°K.)

$$C_p° = 1.66 + 9.198 \times 10^{-2}T - 3.304 \times 10^{-5}T^2 \quad (2)$$

2-Methyl-2-butene: (±0.1%, 319–471°K.)

$$C_p° = 3.10 + 7.935 \times 10^{-2}T - 1.860 \times 10^{-5}T^2 \quad (3)$$

Heats of vaporization were measured at three different temperatures for each of the three compounds, and the values obtained are tabulated in Table II. It is believed that the accuracy of these heat of vaporization values is about 0.1%. The following equations may be used for interpolation within the temperature intervals covered by the experimental measurements:

1-Pentene: (284–303°K.)

$$\Delta H_{\text{vap.}} = 8869 - 5.440T - 1.304 \times 10^{-2}T^2 \quad (4)$$

2-Methyl-1-butene: (278–304°K.)

$$\Delta H_{\text{vap.}} = 8809 - 3.610\,T - 1.745 \times 10^{-2}T^2 \quad (5)$$

2-Methyl-2-butene: (290–312°K.)

$$\Delta H_{\text{vap.}} = 8809 - 2.604\,T - 1.760 \times 10^{-2}T^2 \quad (6)$$

TABLE I

VAPOR HEAT CAPACITIES IN CAL./DEG./MOLE

1 cal. = 4.1833 int. joules; mol. wt. = 70.13; 0°C. = 273.16°K.

			1-Pentene		
T, °K.	311.09	357.51	402.32	436.01	471.08
C_p (760 mm.)	27.660	30.540	33.466	35.636	37.846
C_p (371 mm.)	27.246	30.340	33.347	35.553	37.768
$C_p°$	26.85	30.15	33.24	35.47	37.69
			2-Methyl-1-butene		
T, °K.	320.66	362.51	407.11	453.41	502.21
C_p (758 mm.)	28.405	30.987	33.820	36.718	39.585
C_p (610 mm.)	28.264				
C_p (274 mm.)	27.992	30.790	33.684	36.640	39.540
$C_p°$	27.76	30.68	33.61	36.60	39.52
			2-Methyl-2-butene		
T, °K.	319.04	362.37	402.26	436.18	471.09
C_p (758 mm.)	27.535	29.894	32.315	34.397	36.471
C_p (466 mm.)	27.156				
C_p (337 mm.)	26.978	29.613	32.147	34.279	36.396
$C_p°$	26.53	29.39	32.01	34.19	36.34

TABLE II

HEATS OF VAPORIZATION

1 cal. = 4.1833 int. joules; mol. wt. = 70.13; 0°C. = 273.16°K.

Compound	T, °K.	No. expts.	$\Delta H_{\text{vap.}}$ cal./mole
	283.96	5	6273 ± 5[a]
1-Pentene	298.16	3	6088 ± 5
	303.13	3	6022 ± 4
	277.96	3	6457 ± 1
2-Methyl-1-butene	298.16	4	6181 ± 8
	304.32	4	6094 ± 3
	289.90	3	6575 ± 2
2-Methyl-2-butene	298.16	3	6468 ± 2
	311.73	3	6287 ± 1

[a] Maximum deviation from mean.

Vapor Pressures.—For measuring the vapor pressures of the three pentenes, a pair of differential ebulliometers was employed. By means of these, the boiling points of the compounds were compared with the boiling points of water in a closed system under nitrogen gas at various predetermined pressures between 180 and 2100 mm. of mercury. Some minor modifications were made in the differential ebulliometer apparatus described in a prior publication from this Laboratory,[9] in order to adapt it for measurements with low-boiling compounds. (a) In order to determine condensation temperatures lower than room temperature, the section of the sample ebulliometer containing the thermometer well for measuring condensation temperatures was cooled by surrounding it with a coil of copper tubing through which was circulated an ethylene glycol–water mixture from a refrigeration unit. With this arrangement it was possible to satisfactorily determine condensation temperatures as low as 10°. (b) A condenser cooled with solid carbon dioxide was placed above the sample ebulliometer, to supplement the regular condenser which was

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[4] Waddington, Todd and Huffman, THIS JOURNAL, **69**, 22 (1947).

[5] Waddington and Douslin, *ibid.*, **69**, 2275 (1947).

[6] The 1-pentene sample was loaned by the Phillips Petroleum Corporation through the coöperation of Mr. F. E. Frey. The 2-methyl-2-butene and 2-methyl-1-butene samples were supplied by Dr. W. G. Lovell of the Research Laboratories Division of General Motors Corporation.

[7] Determined by H. J. Coleman of this station.

[8] Scott, Waddington, Smith and Huffman, *J. Chem. Phys.*, **15**, 565 (1947).

[9] Waddington, Knowlton, Scott, Oliver, Todd, Hubbard, Smith and Huffman, THIS JOURNAL, **71**, 797 (1949).

TABLE III

VAPOR PRESSURES IN MM.

Water		1-Pentene		2-Methyl-1-butene		2-Methyl-2-butene	
Boiling pt., °C.	P	Boiling pt., °C.	P (calcd., Eq. 7)	Boiling pt., °C.	P (calcd., Eq. 8)	Boiling pt., °C.	P (calcd., Eq. 9)
65	187.57					3.042	187.56
70	233.72	−0.159	233.78	1.155	233.74	8.008	233.81
75	289.13	4.751	289.11	6.054	289.13	12.987	289.03
80	355.22	9.706	355.14	10.993	355.21	18.033	355.26
85	433.56	14.706	433.45	15.973	433.54	23.103	433.52
90	525.86	19.750	525.75	20.996	526.86	28.220	525.87
95	633.99	24.834	633.86	26.062	634.06	33.373	633.97
100	760.00	29.967	759.98	31.162	759.96	38.567	759.96
105	906.06	35.142	906.17	36.308	906.02	43.806	906.15
110	1074.6	40.359	1074.8	41.500	1074.7	49.078	1074.6
115	1268.0	45.614	1268.2	46.728	1268.0	54.399	1268.2
120	1489.1	50.914	1489.3	52.005	1489.3	59.753	1489.2
125	1740.8	56.253	1740.6	57.320	1740.9	65.151	1740.8
130	2026.0	61.641	2025.7	62.675	2025.8	70.590	2025.9

cooled with the cold ethylene glycol–water mixture. (c) To prevent contamination of the water by diffusion of pentene vapors into the water ebulliometer, an ordinary reflux condenser was introduced above this ebulliometer and used instead of the total-condensation condenser. This arrangement was effective in excluding pentene vapors from the water ebulliometer, as was evidenced by the fact that following a series of measurements, the boiling and condensation temperatures of the water did not differ by more than 0.001° at the normal boiling point.

The 1-pentene used for the vapor-pressure studies was A.P.I.–N.B.S. sample B[10] having a reported impurity of 0.18 ± 0.12 mole per cent., as determined by the time–temperature freezing-point method. The 2-methyl-1-butene was the same A.P.I.–N.B.S. sample[10] that was used for low-temperature studies by Todd, Oliver and Huffman,[3] who found the impurity to be 0.58 ± 0.05 mole per cent. from the change of melting point with fraction melted. The 2-methyl-2-butene was the same sample that was used for the vapor heat capacity and heat of vaporization measurements.

The differences between the boiling and condensation temperatures observed for these samples at their normal boiling points were as follows: 1-pentene, 0.013°; 2-methyl-1-butene, 0.013°; 2-methyl-2-butene, 0.016°. The materials therefore all fall into group IV on Swietoslawski's scale of degree of purity[11] (difference in boiling and condensation temperatures, 0.005–0.020°). It is likely that the accuracy of the vapor pressure measurements reported here is limited by the purity of the samples rather than by the accuracy of the actual ebulliometric measurements.

The results of the vapor pressure measurements are tabulated in Table III. The values of the vapor pressure of water (column 2) were taken from the compilation of Osborne, Stimson and Ginnings.[12] The experimental data for the three compounds were fitted to Antoine equations by the method of least squares,[13] giving equal weight to each experimental point. The equations obtained are:

$$\text{1-Pentene:}\quad \log_{10}P = 6.85487 - \frac{1049.000}{t + 233.994} \tag{7}$$

$$\text{2-Methyl-1-butene:}\quad \log_{10}P = 6.87314 - \frac{1053.780}{t + 232.788} \tag{8}$$

$$\text{2-Methyl-2-butene:}\quad \log_{10}P = 6.91562 - \frac{1095.088}{t + 232.842} \tag{9}$$

Values of the vapor pressures calculated by means of these equations are listed in columns 4, 6 and 8 of Table III for comparison with the observed values given in column 2. The normal boiling points computed from these equations are: 1-pentene, 29.97°; 2-methyl-1-butene, 31.16°; 2-methyl-2-butene, 38.57°.

So far as the authors are aware, the only other vapor-pressure data for any of these three compounds are Lamb and Roper's values for 2-methyl-2-butene covering the range −79 to +18°.[14] Where the two sets of measurements overlap, Lamb and Roper's values are approximately 1% higher than those calculated from equation (9) of this paper.

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(10) These samples of A.P.I.–N.B.S. hydrocarbons have been made available by the American Petroleum Institute and the National Bureau of Standards through A. P. I. Research Project 44 on the "Collection, analysis and calculation of data on the properties of hydrocarbons." The samples were purified at the National Bureau of Standards by A. P. I. Research Project 6 on the "Analysis, purification, and properties of hydrocarbons," under the supervision of Frederick D. Rossini, from material supplied by the following laboratories: 1-pentene, by the Phillips Petroleum Company, Bartlesville, Oklahoma; 2-methyl-1-butene, by the General Motors Corporation through the courtesy of T. A. Boyd and Wheeler G. Lovell.

(11) Swietoslawski, "Ebulliometric Measurements," Reinhold Publishing Corp., New York, N. Y., 1945, p. 80.

(12) Osborne, Stimson and Ginnings, *J. Research, Natl. Bur. Standards*, **23**, 261 (1939).

(13) Willingham, Taylor, Pignocco and Rossini, *J. Research Natl. Bur. Standards*, **35**, 219 (1945).

(14) Lamb and Roper, THIS JOURNAL, **62**, 806 (1940).

TABLE IV

SECOND VIRIAL COEFFICIENTS AND VALUES OF $(\partial C_p/\partial P)_T$

1-Pentene			2-Methyl-1-butene			2-Methyl-2-butene		
T, °K.	B, liters obs.	calcd.	T, °K.	B, liters obs.	calcd.	T, °K.	B, liters obs.	calcd.
283.96	−1.265	−1.276	277.96	−1.258	−1.337	289.90	−1.365	−1.382
298.16	−1.143	−1.143	298.16	−1.163	−1.146	298.16	−1.276	−1.278
303.13	−1.099	−1.099	304.32	−1.117	−1.100	311.73	−1.143	−1.134
T, °K.	$(\partial C_p/\partial P)_T$[a] obs.	calcd.	T, °K.	$(\partial C_p/\partial P)_T$[a] obs.	calcd.	T, °K.	$(\partial C_p/\partial P)_T$[a] obs.	calcd.
311.09	0.81	0.82	320.66	0.65	0.65	319.04	1.01	0.99
357.51	.39	.40	362.51	.31	.34	362.37	0.51	.51
402.32	.22	.23	407.11	.21	.19	402.26	.30	.31
436.01	.16	.16	453.41	.12	.12	436.18	.21	.21
471.08	.15	.11	502.21	.07	.07	471.09	.14	.15

[a] Units: cal./deg./mole/atmos.

Gas Imperfection and Second Virial Coefficients.—Values of the second virial coefficient, B, in the equation of state $PV = RT + BP$ were obtained from the heat of vaporization and vapor pressure data for each of the three compounds by means of the relation

$$B = [\Delta H_{\text{vap.}}/T(\mathrm{d}P/\mathrm{d}T)] - RT/P + v_L$$

where v_L is the molar volume of the liquid. Also the data for the variation of the vapor heat capacity with pressure yielded values of the second derivative of B with respect to temperature, since $(\partial C_p/\partial P)_T = -T(\partial^2 B/\partial T^2)_P$. These data were correlated by means of empirical equations for the second virial coefficients

$$\text{1-Pentene:} \quad B = -0.219 - 0.0530e^{850/T} \text{ liters} \quad (10)$$

$$\text{2-Methyl-1-butene:} \quad B = -0.410 - 0.0304e^{950/T} \text{ liters} \quad (11)$$

$$\text{2-Methyl-2-butene:} \quad B = -0.107 - 0.0572e^{900/T} \text{ liters} \quad (12)$$

The constants of these equations were evaluated by the method described previously.[8] These empirical equations are useful for testing the internal consistency of the heat of vaporization and vapor pressure measurements, and for obtaining the gas imperfection corrections to the entropies of vaporization, but they would be of questionable reliability for extrapolation to temperatures beyond the range within which the second virial coefficients have been measured.

In Table IV are listed the values of the second virial coefficients and of $(\partial C_p/\partial P)_T$ obtained from the experimental data and, for comparison, the values calculated from equations 10, 11 and 12. The observed and calculated values of B are in satisfactory agreement except for the case of 2-methyl-1-butene at 277.96°K. This temperature is near the lower end of the range covered by the vapor pressure measurements, where $\mathrm{d}P/\mathrm{d}t$ and therefore B are more sensitive to minor inaccuracies in the observed vapor pressures, which fact may account for the poorer agreement here.

Entropy of the Vapors.—The entropy of each of the three compounds in the vapor state was calculated from Todd, Oliver and Huffman's values of the liquid entropies,[3] and the heat of vaporization, vapor pressure, and gas imperfection data obtained in this research. The results of these calculations are summarized in Table V. For calculating the gas imperfection corrections, which are given by $\int^P (\partial B/\partial T)_P \,\mathrm{d}P$ in terms of the second virial coefficient, equations 10, 11 and 12 were used.

TABLE V

ENTROPY OF VAPORS

1-Pentene

T, °K.	283.96	298.16	303.13
Entropy of liquid	60.96	62.75	63.37
Vaporization, $\Delta H_{\text{vap.}}/T$	22.11	20.42	19.87
Compression, $R \ln P/760$	−1.42	−0.35	0.00
Gas imperfection	0.13	0.18	0.20
Entropy of ideal gas at 1 atm.	81.78 ±0.25	83.00 ±0.25	83.44 ±0.25

2-Methyl-1-butene

T, °K.	277.96	298.16	304.32
Entropy of liquid	58.11	60.70	61.47
Vaporization, $\Delta H_{\text{vap.}}/T$	23.23	20.73	20.03
Compression, $R \ln P/760$	−2.03	−0.44	0.00
Gas imperfection	0.10	0.15	0.17
Entropy of ideal gas at 1 atm.	79.41 ±0.20	81.14 ±0.20	81.67 ±0.20

2-Methyl-2-butene

T, °K.	289.90	298.16	311.73
Entropy of liquid	58.98	60.00	61.64
Vaporization, $\Delta H_{\text{vap.}}/T$	22.68	21.69	20.17
Compression, $R \ln P/760$	−1.62	−0.97	0.00
Gas imperfection	0.15	0.18	0.23
Entropy of ideal gas at 1 atm.	80.19 ±0.20	80.90 ±0.20	82.04 ±0.20

Discussion

Comparison with Estimates by the Method of Increments.—It is interesting to compare the calorimetric values of entropy and heat capacity found in this investigation with the values previously estimated by Kilpatrick, Prosen, Pitzer and Rossini.[15] These estimates were made by adding appropriate structural increments to the corresponding functions of certain of the butenes, taking into consideration differences of symmetry number and barriers to internal rotation. Such a comparison is made in Table VI for the entropy at 298.16°K. and the heat capacity at 400°K. Considering that the estimates of Kilpatrick, *et al.*, were made before calorimetric data were available for these compounds, the comparison is quite satisfactory and leads to increased confidence in the "method of increments" as a means of estimating thermodynamic functions when calorimetric data are lacking.

TABLE VI

	1-Pentene		2-Methyl-1-butene		2-Methyl-2-butene	
	$S^\circ_{298.16}$	C_{p400}	$S^\circ_{298.16}$	C°_{p400}	$S^\circ_{298.16}$	C°_{p400}
Calorimetric (this research)	83.00	33.06[a]	81.15	33.16[b]	80.90	31.86[c]
Calculated (K, P, P, R)	83.08	34.20	81.73	33.71	80.90	32.22

[a,b,c] Using interpolation equations (1), (2) and (3), respectively.

Vibrational Assignment for 2-Methyl-2-butene.—The molecule of 2-methyl-2-butene consists of a rigid frame with attached symmetrical tops, and it was found possible to treat this compound by detailed statistical mechanical methods. The available spectroscopic data[16–24] were examined and a vibrational assignment was made, which, while not complete or certain in all details, is probably correct for the thermodynamically important low frequencies and statistically correct for the higher frequencies. The pertinent spectroscopic data are summarized in Table VII. The Raman displacements listed are those reported by Gerding and Van der Vet,[20] or Fenske and co-workers,[21] or both, with polarization data by the latter group of workers. The infrared bands which are listed are those reported by the Socony–Vacuum Laboratories.[24]

TABLE VII

SPECTRA OF 2-METHYL-2-BUTENE BELOW 1700 CM.$^{-1}$

Raman (liquid) $\Delta\nu$ cm.$^{-1}$	Infrared (gas) ν cm.$^{-1}$	Assignment
202 (v. w.)		Int. rot.
250 (w.)		Skeletal δ, A′
296 (v. w.)		See text
342 (v. w.)		Skeletal δ, A″
386 (m.) pol.		Skeletal δ, A′
444 (m.) depol.		Skeletal δ, A″
526 (s.) pol.		Skeltal δ, A′
680 (v. w.)		2 × 342 = 684
768 (s.) pol.		C–C v, A′
802 (w.) depol.	801 (s.)	C–H wag, A″
	808 (s.)	C–C v, A′
894 (v. w.)		CH_3 wag, A″
953 (v. w.)	958 (m.)	C–C v, A′
	990 (m.)	CH_3 wag, A″
1034 (w.) pol.	1037 (m.)	CH_3 wag, A′
	1047 (m.)	
1053 (w.) pol.		2 × 526 = 1052
1072 (w.) depol.?	1060 (m.)	CH_3 wag, A″
1107 (v. w.)	1104 (s.)	CH_3 wag, A′
	1111 (s.)	
1153 (v. w.)		386 + 768 = 1154
1210 (v. w.)	1212 (m.)	444 + 768 = 1212
	1217 (m.)	CH_3 wag, A′
	1227 (m.)	
1284 (v. w.)		526 + 768 = 1294
1336 (m.) pol.		C–H wag, A′
1383 (m.) pol.	1381 (s.)	CH_3 δ sym., A′
	1389 (s.)	
1447 (s.) depol.	1453 (s.)	CH_3 δ unsym. A′ & A″
	1522 (m.)	526 + 990 = 1516
	1603 (w.)	2 × 801 = 1602
1677 (s.) pol.	1681 (w.)	C=C v, A′

The 2-methyl-2-butene molecule has C_s symmetry and its 36 vibrations fall into two symmetry classes, A′ and A″, both of which are permitted in both the Raman and infrared spectra. The former gives rise to polarized and the latter to depolarized Raman lines. The contours of the infrared bands, when sufficiently resolved, are also useful in assigning observed frequencies to the proper symmetry class. The molecule of 2-methyl-2-butene is an asymmetric top, from whose moments of inertia (*cf. seq.*) the asymmetry parameters of Badger and Zumwalt[25] may be calculated to be ρ = 1.44 and S = −0.61. The A″ frequencies give rise to bands with a C-type contour, which, for these values of the parameters, will consist of a strong Q branch and weak, diffuse P and R branches. The bands at 990 and 1060 cm.$^{-1}$ appear to be of this type. The A′ frequencies give rise to bands whose contours are hybrids of the A and B types. The double minimum contour of the bands with centers at about 953, 1042, 1107, 1222 and 1385 cm.$^{-1}$ seems compatible with such a hybrid A and B type contour. The contour of the strong band at about 800 cm.$^{-1}$ is best explained as arising from a strong C type band with a second weaker band superimposed on the high frequency side.

The vibrational assignment for 2-methyl-2-butene is given in Table VIII. For determining in which region of the spectrum to look for the fre-

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(15) Kilpatrick, Prosen, Pitzer and Rossini, *J. Research Natl. Bur. Standards*, **36**, 559 (1946).

(16) Weiler, *Z. Physik*, **69**, 586 (1931) [as pointed out by Bourguel and Piaux, ref. 17, Weiler's "amylene" was apparently 2-methyl-2-butene and not 3-methyl-1-butene as he supposed].

(17) Bourguel and Piaux, *Bull. soc. chim.*, **51**, 1041 (1932).

(18) Gehman and Osterhof, THIS JOURNAL, **58**, 215 (1936).

(19) Thompson and Sherrill, *ibid.*, **58**, 745 (1936).

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(21) Fenske, Braun, Wiegand, Quiggle, McCormick and Rank, *Ind. Eng. Chem., Anal. Ed.*, **19**, 700 (1947).

(22) Thompson and Torkington, *Proc. Roy. Soc.* (*London*), **A184**, 3 (1945).

(23) American Petroleum Institute Research Project 44 at the National Bureau of Standards, Catalog of Infrared Spectrograms. Serial No. 26, 2-methyl-2-butene (gas), contributed by the Shell Development Co., Emeryville, Calif.

(24) *Ibid.*, Serial No. 361, 2-methyl-2-butene (gas), contributed by the Socony-Vacuum Oil Co., Paulsboro, N. J.

(25) Badger and Zumwalt, *J. Chem. Phys.*, **6**, 711 (1938).

quency arising from a particular type of motion, Kilpatrick and Pitzer's[26] vibrational assignments for the three rigid-frame butenes proved to be very helpful. Average or conventional values were used for C—H stretching and CH_3 bending frequencies which are not resolved in the spectrum of a molecule of this complexity. There are Raman lines and infrared bands in the spectrum of 2-methyl-2-butene at approximately the frequencies adopted for the conventional values.

TABLE VIII

VIBRATIONAL ASSIGNMENT OF 2-METHYL-2-BUTENE

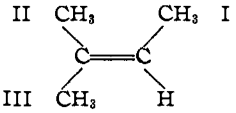
IR, observed in infrared spectrum; R, observed in Raman spectrum; (c), conventional value; (p), polarized; (d) depolarized.

Type vibration	A′	A″
C–H v (ethylenic)	3050 (c)	
C–H v (methyl)	(6) 2950 (c)	(3) 2950 (c)
C=C v	1680 IR, R(p)	
C–C v	768 R(p)	
	808 IR	
	953 IR, R	
CH_3 δ unsym.	(3) 1450 (c)	(3) 1450 (c)
CH_3 δ sym.	(3) 1380 (c)	
CH_3 wagging	1042 IR, R(p)	894 R
	1107 IR, R	990 IR
	1222 IR	1060 IR, R(d)
C–H wagging	1336 R(p)	801 IR, R(d)
Skeletal δ	250 R	342 R
	386 R(p)	444 R(d)
	526 R(p)	

The thermodynamically important skeletal bending frequencies would be expected to appear in the region of the spectrum below 600 cm.$^{-1}$. There are five such modes of motion, and seven Raman lines with frequencies less than 600 cm.$^{-1}$ have been observed. Intensity considerations indicate that four of these, 250, 386, 444 and 526 cm.$^{-1}$ are fundamentals. It is difficult to account for the weak Raman line at 680 cm.$^{-1}$ unless the fifth fundamental is taken as 342 cm.$^{-1}$, in which case the 680 cm.$^{-1}$ frequency is its first overtone. The two left-over frequencies, 202 and 296 cm.,$^{-1}$ probably arise from internal torsional motions of the methyl groups. The former may be the fundamental of one of the torsional modes; the latter seems somewhat high for such a fundamental, but may well be a difference-combination involving a lower frequency torsional motion.

The assignment of the frequencies between 600 and 1350 cm.$^{-1}$ is fairly definite except for the weak Raman line at 894 cm.$^{-1}$ which may be an overtone (2 × 444 = 888) instead of a fundamental frequency. The observed frequencies that were not assigned as fundamentals can readily be accounted for as overtones or sum-combinations as shown in Table VII.

Thermodynamic Functions of 2-Methyl-2-butene.—Since the molecule of a 2-methyl-2-butene consists of a rigid frame with attached symmetrical tops, it was treated by the method of Pitzer and Gwinn.[27] The contributions of translation, over-all rotation, and vibration to the thermodynamic functions were calculated by the usual harmonic-oscillator rigid-rotator approximation. To obtain the moments of inertia, the following bond distances and angles were assumed: C═C, 1.353 Å.; C—C, 1.54 Å.; C—H (ethylenic), 1.071 Å.; C—H (methyl), 1.09 Å.; all angles about the doubly-bonded carbon atoms, 120°; all methyl group bond angles, 109° 28′. The three principal moments of inertia are 1.070×10^{-38}, 2.314×10^{-38}, and 3.225×10^{-38} g. cm.^{2} The axis of smallest moment makes an angle of 35° 37′ with the C═C bond. The reduced moments for internal rotation of the three methyl groups (numbered as in the structural formula below) are 5.056×10^{-40} g. cm.^{2} for methyl groups I and III and 5.176×10^{-40} g. cm.^{2} for methyl group II. The symmetry number is one. The values of the fundamental



constants given by Wagman, *et al.*,[28] and 1948 atomic weights were used in the calculations.

In treating the internal rotations of the three methyl groups, independent threefold cosine-type barriers were assumed. This approximation neglects the relatively strong potential interactions which undoubtedly exist between adjacent methyl groups, but any more refined treatment to take into account these potential interactions does not seem feasible at the present time. As the effective barrier heights are different for each of the three methyl groups, it was not practical to evaluate all of them from the thermal data alone. It was assumed that the effective barrier height for methyl group I was the same as for a methyl group in *cis*-2-butene, namely, 450 cal./mole,[29] and that the effective barrier height for methyl group III was the same as for a methyl group in isobutene, namely, 2350 cal./mole.[29] It was then found that satisfactory agreement was obtained with the calorimetric entropy and vapor heat capacity data if the effective barrier height for methyl group II was taken to be zero (that is, free internal rotation). A comparison of the calorimetric data with the values computed using these effective barrier heights is given in Table IX. The good check between the observed and calculated values is evidence of the essential correctness of the vibration assignment and barrier heights used in the calculations, at least in a statistical sense.

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(26) Kilpatrick and Pitzer, *J. Research Natl. Bur. Standards*, **38**, 191 (1947).

(27) Pitzer and Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

(28) Wagman, Kilpatrick, Taylor, Pitzer and Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

(29) Kilpatrick and Pitzer, *J. Research Natl. Bur. Standards*, **37**, 163 (1946).

TABLE IX

2-METHYL-2-BUTENE

Entropy, cal./deg./mole

T, °K.	289.90	298.16	311.73
Calorimetric value	80.19	80.90	82.04
Calculated[a]	80.22	80.92	82.05

Vapor Heat Capacity, cal./deg./mole

T, °K.	319.04	362.37	402.26	436.18	471.09
Calorimetric value	26.53	29.39	32.01	34.19	36.34
Calculated[a]	26.50	29.42	32.07	34.24	36.37

[a] For effective barrier heights for methyl rotations of 450, zero, and 2350 cal./mole.

Table X lists values of the free-energy function, heat-content function, entropy, and heat capacity of 2-methyl-2-butene vapor at selected temperatures up to 1500°K. These were calculated using the moments of inertia, vibrational frequencies, and barrier heights given previously.

TABLE X

THERMODYNAMIC FUNCTIONS OF 2-METHYL-2-BUTENE

T, °K.	$(H^\circ_0 - F^\circ_T)/T$, cal./deg./mole	$H^\circ_T - H^\circ_0$ kcal./mole	S°_T, cal./deg./mole	C°_{pT}, cal./deg./mole
298.16	64.71	4.833	80.92	25.10
300	64.79	4.878	81.05	25.22
400	69.87	7.736	89.21	31.93
500	74.53	11.25	97.02	38.07
600	78.89	15.32	104.43	43.42
700	83.06	19.90	111.49	48.04
800	87.03	24.91	118.17	52.05
900	90.85	30.29	124.50	55.52
1000	94.52	36.00	130.52	58.55
1100	98.06	41.99	136.23	61.16
1200	101.46	48.22	141.64	63.45
1300	104.75	54.67	146.80	65.42
1400	107.91	61.31	151.70	67.14
1500	110.99	68.10	156.39	68.63

The entries in the table are internally consistent to the number of significant figures given, but the actual uncertainty in the values may be several tenths of a unit at the higher temperatures.

Rotational Tautomers of 2-Methyl-1-butene.—The molecule of 2-methyl-1-butene can exist in two tautomeric forms which differ with respect to the angle of rotation of the ethyl group. The complexity of the spectra of this compound indicates that both forms are present in appreciable amounts at ordinary temperatures. If it were known to which of the two forms each observed vibrational frequency corresponds (as could be ascertained by studying the relative intensities of the Raman lines as a function of temperature) it might be possible to make vibrational assignments for both forms and then use the calorimetric data reported here to obtain information about the energy difference between the two forms.

Acknowledgment.—Thanks are tendered to Wf. Roberts, formerly of this station, for his assistance with some of the measurements.

Summary

The following thermodynamic properties were determined for 1-pentene, 2-methyl-1-butene, and 2-methyl-2-butene: heats of vaporization at three temperatures, vapor heat capacities at five temperatures, vapor pressures and normal boiling points, second virial coefficients, values of $(\partial C_p/\partial P)_T$, and the entropies of the vapors at three temperatures.

A vibrational assignment was made for 2-methyl-2-butene, and the free energy function, heat content function, entropy and heat capacity of this substance were computed for selected temperatures up to 1500°K. by statistical mechanical methods.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Thermal Data on Organic Compounds. XXIV. The Heat Capacities, Entropies and Free Energies of *cis*- and *trans*-Decahydronaphthalene[1]

BY GEORGE S. PARKS AND JOHN A. HATTON

A comprehensive study of the physical-chemical properties of *cis*- and *trans*-decahydronaphthalene was initiated about twelve years ago by Professor W. F. Seyer[2] of the University of British Columbia. With the aid of several students he prepared these compounds in rather pure form and measured their freezing points, densities, refractive indices, surface tensions, viscosities, vapor pressures and dielectric constants. In 1940 he also gave samples of his purified materials to Professor E. C. Gilbert of Oregon State College for the accurate measurement of the heats of combustion[3] and to one of us (G. S. P.) for the determination of the heat capacities at low temperatures. While we completed these last measurements in 1941, the publication of the results has been delayed by various wartime and post-war exigencies.

In the present paper we shall present compara-

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[1] Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the San Francisco Meeting, March, 1949.

[2] W. F. Seyer and co-workers, THIS JOURNAL, **60**, 2125 (1938); **63**, 2425 (1941); **64**, 1912 (1942); **67**, 328 (1945); **70**, 802 (1948).

[3] G. F. Davies and E. C. Gilbert, *ibid.*, **63**, 1585 (1941).