TABLE III

MONOISOTOPIC MASS SPECTRA OF THE BORON TRIHALIDES

RELATIVE ABUNDANCE

Species	BCl_3		BBr_3		BI_3	
BX_3^+	BCl_3^+	36.11	BBr_3^+	37.0	BI_3^+	Out of range
BX_3^{++}	BCl_3^{++}	1.11	BBr_3^{++}	5.31	BI_3^{++}	2.19
BX_2^+	BCl_2^+	100	BBr_2^+	100	BI_2^+	100
BX_2^{++}	BCl_2^{++}	3.71	BBr_2^{++}	0.27	BI_2^{++}	0
BX^+	BCl^+	7.63	BBr^+	48.91	BI^+	21.95
BX^{++}	BCl^{++}	0	BBr^{++}	1.03	BI^{++}	9.50
B^+	B^+	2.94	B^+	0.51	B^+	8.96
					Also evidence of BI_3^{+++} BI_3^{++++} BI_3^{+++++}	

chosen BY_3 molecule (in which the –Y's are different substituent groups) where the $I(BY_2)$ has been previously calculated from some known thermochemical data combined with electron impact experiments. There is also reason to believe that this approach can be extended to other types of compounds such as aluminum and silicon compounds in which there is a great deal of interest and a great scarcity of thermochemical data.

There are two instances in which this method should be of immediate interest in the field of boron compounds. First, to determine the B–X bond dissociation energy in molecules of the type BR_2X. Apparently the B–X bond dissociation energy in these molecules is not the same as the $(B-X)_{av}$ bond dissociation energy derived from BX_3 molecules. Second, to determine bond dissociation energies in BR_2R' molecules since a new method of preparation has made these mixed alkyl derivatives quite easy to prepare.

Finally, for comparison purposes, the fragmentation patterns for the boron trihalides were obtained at a constant ionizing voltage—70 e.v. From these, the monoisotopic mass spectra of the boron trihalides were calculated.

The values for BCl_3 check well with literature values.

It is of interest to note the greater abundance of multiply charged ions in the Br and I compounds. Evidence has been found for BI_3 ions with +3 and +4, and even +5 charges. This is in agreement with observation of multiply charged ions of Br and I compounds in radiation studies.[25]

[25] R. H. Luebbe, Jr., and J. E. Willard, *J. Chem. Phys.*, **29**, 124 (1958).

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[CONTRIBUTION NO. 81 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR]

Thermodynamic Properties, Vibrational Assignment and Rotational Conformations of 2-Methyl-1-butene

BY J. P. MCCULLOUGH AND D. W. SCOTT

RECEIVED OCTOBER 15, 1958

In a continuation of thermodynamic studies of monoölefins, values of the following thermodynamic properties of 2-methyl-1-butene were computed at selected temperatures between 0 and 1500°K.: $(F° - H°_0)/T$, $(H° - H°_0)/T$, $H° - H°_0$, $S°$, $C_p°$, $\Delta Hf°$, $\Delta Ff°$ and log Kf. A detailed vibrational and conformational analysis showed that the compound exists in two spectroscopically distinct conformations, one of which is predominant at room temperature.

In 1946 Kilpatrick, Prosen, Pitzer and Rossini[1] reported values of the thermodynamic properties of the six isomeric pentenes. The results of these authors were calculated from data for lower monoolefins by a method of increments, because values of heat of formation were the only experimental data then available for all isomers. Later, values of the entropy of all six pentenes,[2] the heat of vaporization and vapor heat capacity of three pentenes, and the thermodynamic functions of 2-methyl-2-butene[3] were reported from this Laboratory.

This paper presents values of the chemical thermodynamic properties of 2-methyl-1-butene calculated from previously published calorimetric, spectroscopic and molecular structure information. Values of entropy $S°$ and heat capacity $C_p°$, in the ideal gaseous state, taken from ref. 3, are collected in Table I. These results were used in the vibrational and conformational analysis of 2-methyl-1-butene.

Calculation of Thermodynamic Functions

For calculating the thermodynamic functions by the methods of statistical mechanics, a detailed vibrational assignment and an analysis of the effect of internal rotation were required. As previously noted,[3] 2-methyl-1-butene may exist in two spectroscopically distinct rotational conformations. Therefore, it was necessary to make a complete vibrational assignment for one conformation from spectroscopic data and to determine the relative stabilities of the two conformations from calorimetric data.

TABLE I

OBSERVED AND CALCULATED MOLAL ENTROPY AND HEAT CAPACITY OF 2-METHYL-1-BUTENE IN THE IDEAL GASEOUS STATE

	Entropy $S°$, cal. deg.$^{-1}$			Heat capacity $C_p°$, cal. deg.$^{-1}$	
T, °K.	Obsd.[a]	Calcd.	T, °K.	Obsd.[b]	Calcd.
277.96	79.41	79.39	320.66	27.76	27.79
298.16	81.14	81.15	362.51	30.68	30.66
304.32	81.67	81.69	407.11	33.61	33.65
			453.41	36.60	36.60
			502.21	39.52	39.51

[a] From Table V, ref. 3. [b] From Table I, ref. 3.

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[1] J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **36**, 559 (1946).

[2] S. S. Todd, G. D. Oliver and H. M. Huffman, THIS JOURNAL, **69**, 1519 (1947).

[3] D. W. Scott, G. Waddington, J. C. Smith and H. M. Huffman, *ibid.*, **71**, 2767 (1949).

Moments of Inertia.—The molecular structure of 2-methyl-1-butene has not been determined experimentally. The assumption was made, and later shown to be consistent with the thermal data, that the most stable conformation of this molecule is that shown in Fig. 1, in which the ethyl group is rotated 60° out of the plane of the rest of the molecule. In calculating moments and reduced moments of inertia by the general method of Kilpatrick and Pitzer,[4] the following conventional values of bond distances and angles were used: C=C bond distance, 1.353 Å.; C–C bond distance, 1.54 Å.; paraffinic C–H bond distance, 1.09 Å.; olefinic C–H bond distance, 1.071 Å.; all bond angles about doubly-bonded carbon atoms, 120°; and all other bond angles tetrahedral. For this assumed structure, the product of principal moments of inertia is 7.863×10^{-114} g.^{3} cm.^{6} The reduced moments of inertia for internal rotation, taken as the diagonal elements of the reduced internal rotational kinetic energy matrix,are 5.168×10^{-40} g. cm.^{2} for the branch methyl group, 5.137×10^{-40} g. cm.^{2} for the terminal methyl group, and $12.14_5 \times 10^{-40}$ g. cm.^{2} for the ethyl group.

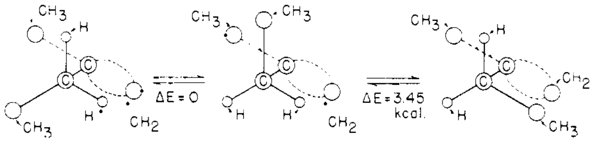

Fig. 1.—The rotational conformations of 2-methyl-1-butene.

Vibrational Assignment.—Several investigators have reported Raman[5] and infrared[6] spectral data for 2-methyl-1-butene; a selected listing of the results is in Table II. There are many more frequencies below 1700 cm.$^{-1}$ than the 26 fundamental vibrations that should appear in this region—a fact originally attributed to the coexistence in significant concentrations of more than one rotational conformation.[3] However, as will be shown in the next section, one conformation is predominant at room temperature, and most of the extra frequencies were assigned as combinations involving fundamentals of the stable form. It is possible that some of the extra frequencies, such as the Raman line at 1679 cm.$^{-1}$, are due to the more intense vibrations of the high-energy conformation.

The frequencies selected as fundamentals of the stable conformation are listed in the fourth column of Table II. For comparison, the assignment of Kilpatrick and Pitzer[7] for 2-methyl-1-propene (isobutene) is listed in the fifth column. The agreement for vibrations related to those of isobutene is excellent. The remaining fundamentals of 2-methyl-1-butene are those of the ethyl group, and these fundamentals also are found in characteristic regions of the spectrum.

Barriers to Internal Rotation and Conformational Analysis.—There are three internal rotational degrees of freedom for 2-methyl-1-butene, involving two methyl and one ethyl rotations. The heights of the barriers to internal rotation of the methyl groups were selected as 2400 and 3400 cal. mole^{-1} by analogy with those in isobutene and 1-butene.[8] The barrier to internal rotation of the ethyl group was assumed to be of the form

$$\begin{aligned} V(\mathrm{C_2H_5}) &= {}^1/_2V_0(1 + \cos 3\phi),\ -2\pi/3 < \phi < 2\pi/3 \\ &= {}^1/_2V_0(1 + \cos 3\phi) + \Delta E,\ 2\pi/3 < \phi < 4\pi/3 \end{aligned}$$

where V_0 is the barrier height, ΔE is the difference in energy between the low- and high-energy conformations, and ϕ is the angle of rotation of the ethyl group as measured from that planar configuration in which the methyl groups are in the *cis* position. For this degree of freedom, the contributions to the thermodynamic functions were computed as those for a simple, cosine-type barrier of height V_0 *plus* those due to conversion of molecules from the low-energy to the high-energy conformation. The latter contributions were computed on the assumption that the entropy change for the conversion is $-R \ln 2$(there are two conformations with low energy and only one with high energy). Values of V_0, 1150 cal. mole^{-1}, and ΔE, 3450 cal. mole^{-1}, were selected simultaneously to give best agreement between calculated and experimental values of $S°$ and $C_p°$. As shown in Table I, agreement within ±0.15% was obtained at all temperatures for which experimental data were available. The method of calculating contributions of internal rotation apparently compensated for effects of anharmonicity, for no anharmonicity corrections were necessary.

Chemical Thermodynamic Properties.—The parameters discussed in the foregoing paragraphs were used in calculating values of the thermodynamic functions at selected temperatures between 0 and 1500°K. The results are in the first six columns of Table III.[9] These values, the value of Prosen and Rossini[10] for the heat of formation at 298.16°K., and values of the thermodynamic functions of graphite and hydrogen gas[11] were used in calculating values of the heat, free energy and common logarithm of the equilibrium constant of formation for 2-methyl-1-butene. The results are in the last three columns of Table III.

Discussion

The results of this investigation provide evidence of the excellent consistency of thermody-

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(5) (a) H. Gerding and A. P. van der Vet, *Rec. trav. chim.*, **64**, 257 (1945), and earlier references cited there. (b) M. R. Fenske, W. G. Braun, R. W. Wiegand, D. Quiggle, R. H. McCormick and D. H. Rank, *Anal. Chem.*, **19**, 700 (1947).

(6) (a) Liquid: N. Sheppard and G. B. B. M. Sutherland, *Proc. Roy. Soc.* (*London*), **A196**, 195 (1949). (b) Vapor: American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology, Catalog of Infrared Spectral Data. Serial Nos. 196, 359 and 560.

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(8) J. E. Kilpatrick and K. S. Pitzer, *ibid.*, **37**, 163 (1946).

(9) The 1951 International Atomic Weights [E. Wichers, This Journal, **74**, 2447 (1952)] and 1951 values of fundamental physical constants [F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, *ibid.*, **74**, 2699 (1952)] were used. The vibrational contributions to the thermodynamic functions were computed by R. W. Smith at the Computation Laboratory, Bureau of Mines, U. S. Department of the Interior, Pittsburgh, Pa. Restricted internal rotation contributions were computed from the tables of K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

(10) E. J. Prosen and F. D. Rossini, *J. Research Natl. Bur. Standards*, **36**, 269 (1946).

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TABLE II

VIBRATIONAL ASSIGNMENT AND SPECTRA FOR 2-METHYL-1-BUTENE, IN CM.$^{-1}$

2-Methyl-1-butene				2-Methyl-1-propene	
	Infrared				
Raman,[a] liq.	Liq.[b]	Vapor[c]	Fundamental[d]	Fundamental[e]	Description
257(1)			257		C—C—C bend.
283(1)			283	378	C—C—C bend.
396(3)			396	391	C—C=C bend.
429(2)			429	431	C—C=C bend.
487(1d)					892 − 396 = 496
529(1)					257 + 283 = 540
563(0)					2 × 283 = 566
599(0)					892 − 283 = 609
633(0)					892 − 257 = 635
672(1/2)		686vw			283 + 396 = 679
709(1)		701vw	701	700	Skel. twist
772(9)	770m	769m	769		CH_2 rock., ethyl
797(1/2)	805m	794m	794	800	C—C str.
885(2)	890s	892s	892	888	CH_2 rock., ethylenic
	920w				1170 − 257 = 913[f]
935(1)	935vw	938w	938		C—C str., ethyl
983(1/2)	990m	984m	984	986	C—C str.
				988	CH_3 rock., methyl
1015(2d)	1015w	1014m	1014	1007	CH_3 rock., methyl
				1053	CH_3 rock., methyl
1083(3)	1075m	1076s	1076	1066	CH_3 rock., methyl
	1105w				396 + 701 = 1097[f]
1141(0)		1130w	1130		CH_3 rock., ethyl
1192(0d)		1170w	1170		CH_3 rock., ethyl
1248(1/2)	1240m	1239s	1239		CH_2 wag., ethyl
	1260w				283 + 984 = 1267
1282(1/2)	1275w	1282m	1282	1280	CH_2 wag., ethylenic
	1290w				396 + 892 = 1288
1322(0)	1320w	1322m	1322		CH_2 twist., ethyl
	1340w				396 + 938 = 1334
1386(2)	1375s	1389s	1389(3)	1380(2) 1390	CH_3 bend., sym. CH_2 bend., ethylenic[g]
1417(5)			1417		CH_2 bend., ethyl[g]
1432(5) 1467(2)	 1455s	 1458s	1432(2) 1458(2)	1450(4)	CH_3 bend., unsym.
1511(0)					283 + 1239 = 1522
1652(10)		1652s	1652	1664	C=C str.
1679(0)					794 + 892 = 1686[f]
	[1700 − 2900 cm.$^{-1}$ region omitted]				
2912(7) 2937(7) 2978(6)		2950s	2950(8)	2950(6)	C—H str., aliphatic
3077(1)		3090s	3090(2)	3050(2)	C—H str., olefinic

[a] Ref. 5; numbers in parentheses indicate relative intensities. [b] Ref. 6a; the letters vw, w, m and s indicate very weak, weak, medium and strong absorption, respectively. [c] Ref. 6b. [d] Chosen as center of vapor-phase absorption bands where possible; numbers in parentheses indicate multiplicities used in calculating thermodynamic functions. [e] Ref. 7. [f] Alternative assignment as fundamental of high-energy conformation is possible; see text. [g] Alternative assignments are 1417 cm.$^{-1}$ for CH_2 bend, ethylenic and 1458 cm.$^{-1}$ for CH_2 bend., ethyl. Sheppard and Sutherland[6a] have proposed the first of these assignments. The difference is unimportant thermodynamically.

namic and molecular structure information now available for light hydrocarbons. The values in Table III differ from those of Kilpatrick, *et al.*,[1] by no more than 1.5%, yet these authors had no experimental data to guide their calculations. This good agreement indicates that the thermodynamic data for lower olefins and the structural ideas on which the incremental calculations were made are reliable. The successful use of transferred barrier heights in the present calculations is further gratifying evidence that present knowledge of the structures and energetics of light hydrocarbons is sound.

In addition to providing new thermodynamic data for 2-methyl-1-butene, this investigation yielded information about unsymmetrical barriers to internal rotation in substituted monoölefins. Although only approximate information about such complex potential energy functions can be obtained from calorimetric data, the results are physically reasonable. The value of V_0 for the ethyl barrier, 1150 cal. mole^{-1}, is low for the barrier about a carbon–carbon single bond, probably because steric interactions raise the minima in the potential energy more than the maxima. The energy difference between rotational conformations,

TABLE III

THE MOLAL THERMODYNAMIC PROPERTIES OF 2-METHYL-1-BUTENE[a]

T, °K.	$(F^\circ_0 - H^\circ_0)/T$, cal. deg.$^{-1}$	$(H^\circ - H^\circ_0)/T$, cal. deg.$^{-1}$	$H^\circ - H^\circ_0$, kcal.	S°, cal. deg.$^{-1}$	C_p°, cal. deg.$^{-1}$	ΔHf°,[b] kcal.	ΔFf°,[b] kcal.	log Kf[b]
0	0	0	0	0	0	− 2.29	− 2.29	Infinite
273.16	−63.00	15.92	4.349	78.92	24.61	− 8.22	+13.66	−10.93
298.16	−64.43	16.72	4.985	81.15	26.28	− 8.68	15.68	−11.49
300.00	−64.53	16.78	5.034	81.31	26.41	− 8.71	15.84	−11.54
400	−69.80	20.04	8.016	89.84	33.20	−10.44	24.29	−13.27
500	−74.63	23.30	11.65	97.93	39.40	−11.89	33.14	−14.49
600	−79.16	26.44	15.86	105.60	44.72	−13.07	42.25	−15.39
700	−83.45	29.39	20.57	112.84	49.26	−13.99	51.55	−16.09
800	−87.56	32.12	25.70	119.68	53.15	−14.69	60.96	−16.65
900	−91.50	34.64	31.18	126.14	56.52	−15.20	70.44	−17.11
1000	−95.27	36.97	36.97	132.24	59.43	−15.52	79.99	−17.48
1100	−98.89	39.14	43.05	138.03	61.96	−15.68	89.54	−17.79
1200	−102.38	41.14	49.37	143.52	64.15	−15.71	99.11	−18.05
1300	−105.75	42.98	55.87	148.73	66.05	−15.69	108.66	−18.27
1400	−109.00	44.69	62.57	153.69	67.71	−15.57	118.23	−18.46
1500	−112.14	46.27	69.40	158.41	69.15	−15.43	127.78	−18.62

[a] To retain internal consistency, some values are given to one more decimal place than is justified by the absolute accuracy. [b] For the reaction 5C(c, graphite) + $5H_2(g) = C_5H_{10}(g)$.

3450 cal. mole^{-1}, also is reasonable, but not much significance can be attached to the actual numerical value. From the value obtained for the energy difference, the concentration of molecules in the high-energy conformation was calculated to be 0.15 mole % at 300°K. This result is consistent with the earlier conclusion that only one or two of the most intense vibrations of the high-energy conformation can be detected spectroscopically.

BARTLESVILLE, OKLAHOMA

[CONTRIBUTION FROM THE GULF RESEARCH & DEVELOPMENT COMPANY]

The Evaluation of Activation Energies Using a Rising Temperature Flow Reactor. The Dehydrogenation of Cyclohexane over WS_2, Pt/Al_2O_3, Cr_2O_3/Al_2O_3, $NiWO_4/Al_2O_3$ and Cr_2O_3

BY JOANNE M. BRIDGES AND G. HOUGHTON

RECEIVED DECEMBER 11, 1957

A rising temperature flow reactor has been used to evaluate the apparent activation energies and kinetics for the dehydrogenation of cyclohexane over WS_2, Pt/Al_2O_3, Cr_2O_3/Al_2O_3, $NiWO_4/Al_2O_3$ and Cr_2O_3. The method has also been used to compare rapidly the activities of the various catalysts. On the basis of equal volumes of catalyst, the order of the activities is approximately $Pt/Al_2O_3 >$ water washed $Cr_2O_3/Al_2O_3 > Cr_2O_3/Al_2O_3 > NiWO_4/Al_2O_3 > Cr_2O_3 > WS_2$. However, on the basis of equal surface areas, the order of the activities is $Pt/Al_2O_3 >$ water washed $Cr_2O_3/Al_2O_3 > Cr_2O_3 > NiWO_4/Al_2O_3 > WS_2 > Cr_2O_3/Al_2O_3$. Electron irradiation from a Van de Graaff accelerator has been found to have no permanent effect on the activity of Pt/Al_2O_3. The thermal cracking of cyclohexane over Vycor wool has been found to proceed in the temperature range 566–700° with an activation energy of 49 ± 5 kcal./g. mole.

Introduction

The literature in the field of catalysis indicates that one of the major obstacles to the investigation and comparison of solid catalysts is the time required to obtain the data. This difficulty has been overcome by the development of what the authors term a rising temperature flow reactor. If the reactor temperature is continuously increased with time at a steady rate of 1–10° per minute in the range 25–700°, the reactor will automatically locate the narrow band of temperature in which catalytic activity measurements can be made. Hauffe, Glang and Engell[1] have used a similar method to compare the activities of various oxides for the decomposition of nitrous oxide. Recently P. Kofstad[2] has used a rising temperature technique to investigate the kinetics of oxidation of various metals. In the present investigation the dehydrogenation of cyclohexane has been chosen for study, since the work of Kasansky and Plate,[3] Herington and Rideal[4] and Balandin and Rubinstein[5] indicates that this reaction is relatively free from complicating side reactions and the production of large quantities of intermediates.

Experimental

Equipment.—A flow diagram for the rising temperature reactor is shown in Fig. 1.

Nitrogen was used as the carrier gas and was purified by passing it over 100 mesh copper gauze at 300° to remove oxygen and then through a drying tube containing magnesium perchlorate. The nitrogen was metered by a cali-

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