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Rotational Isomerism and Thermodynamic Functions of 2-Methylbutane and 2,3-Dimethylbutane. Vapor Heat Capacity and Heat of Vaporization of 2-Methylbutane

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The vapor heat capacity of 2-methylbutane was measured at five temperatures between 317 and 487°K. The experimental values of C_p^0, the heat capacity in the ideal gas state, may be represented by the equation $C_p^0 = -0.01 + 0.10608T - 3.676 \times 10^{-5}T^2$. The heat of vaporization at 279.48, 298.16 and 301.01°K. was found to be 6181, 5937 and 5901 cal./mole, respectively. The following empirical equation for the second virial coefficient, B, in the equation of state $PV = RT + BP$, was obtained from thermal data: $B = -577 - 12.01e^{1150/T}$ cc./mole. Calorimetric entropy and vapor heat capacity data for both 2-methylbutane and 2,3-dimethylbutane were utilized to obtain information about the energy differences between the rotational isomers of these compounds. It was necessary to interpret the spectra and make vibrational assignments for both molecules. It was found that the C_s form of 2-methylbutane is at least several thousand cal./mole less stable than the C_1 form. The energy difference between the rotational isomers of 2,3-dimethylbutane, on the other hand, was found to be very small; spectroscopic data set an upper limit of about 100 cal./mole. Thermodynamic functions were computed by the methods of statistical mechanics for 2-methylbutane and 2,3-dimethylbutane for selected temperatures up to 1500°K.

Introduction

In a study of the Raman spectra of 2-methylbutane and 2,3-dimethylbutane between room temperature and 90°K., Szasz and Sheppard[1] observed very little change in the spectra when the substances were cooled or solidified, and concluded that the energy difference between the two possible rotational isomers of each of these compounds was either less than about 200 cal./mole or else greater than 1000 cal./mole. These investigators suggested that accurate values of vapor heat capacity would serve to distinguish between the two possibilities. The vapor heat capacity of 2,3-dimethylbutane had already been studied in this Laboratory[2] before Szasz and Sheppard's paper was published. The desirability of having vapor heat capacity data for 2-methylbutane as well led to the inclusion of the latter compound in the program of the Bureau of Mines for studying the vapor heat capacities and heats of vaporization of hydrocarbons and related compounds.

The present paper reports experimental vapor heat capacity and heat of vaporization data for 2-methylbutane and presents the interpretation of the calorimetric data for both 2-methylbutane and 2,3-dimethylbutane in terms of the energy differences between the rotational isomers.

Experimental

Apparatus and Material.—Measurements of the vapor heat capacity and heat of vaporization of 2-methylbutane were made with a flow calorimeter and cycling vaporizer as described in previous publications from this Laboratory.[3] The glass cycling vaporizer formerly used has been replaced by a metal vaporizer, which will be described in detail in another publication.

Phillips Petroleum Co. "Pure Grade Isopentane" was used without further purification. The purity of the sample, as determined by the time–temperature freezing-point method, was 99.9 mole per cent. As the impurities were probably hydrocarbons similar in physical properties to 2-methylbutane, it is believed that they had a negligible effect upon the measured heats of vaporization and vapor heat capacities.

Heat of Vaporization and Vapor Heat Capacity.—The values obtained for the heat of vaporization at 279.48°, 298.16° and 301.01°K. were 6181, 5937 and 5901 cal./mole, respectively. These values are averages of three separate determinations at each temperature; the maximum deviations of the individual determinations from the mean were ±2, ±3 and ±1 cal./mole, respectively. The accuracy of these values is probably about ±0.1%. For interpolation within the temperature range covered by the experimental measurements, the following equation may be used

$$\Delta H_{\text{vap.}} = 9816 - 13.005T \qquad (1)$$

Schuman, Aston and Sagenkahn[4] reported 5878 cal./mole for the heat of vaporization of 2-methylbutane at 298.16°K., a value about 1% lower than that found in this investigation.

The heat capacity of 2-methylbutane vapor was determined at two pressures at each of five different temperatures between 317 and 487°K. The results of the measurements are listed in Table I. Values of C_p^0, the heat capacity in the ideal gas state, were obtained at each temperature by linear extrapolation to zero pressure of plots of heat capacity *vs.* pressure. These values of C_p^0, given in Table I, are assigned an accuracy uncertainty of ±0.3%. Over the temperature range covered by the measurements, C_p^0, as a function of temperature, may be represented to better than 0.1% by the empirical equation

$$C_p^0 = -0.01 + 0.10608T - 3.676 \times 10^{-5}T^2 \qquad (2)$$

Gas Imperfection and Second Virial Coefficient.—Values of the second virial coefficient, B, which is defined by the equation of state $PV = RT + BP$, were obtained at three temperatures from the heat of vaporization data of this investigation with the aid of the exact form of the Clapeyron equation. The vapor-pressure equation given in the A.P.I. Tables[5] was used.

The relationship employed was

$$B = [\Delta H_{\text{vap.}}/T(\mathrm{d}P/\mathrm{d}T)] - RT/P + V_L \qquad (3)$$

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[1] G. J. Szasz and N. Sheppard, *J. Chem. Phys.*, **17**, 93 (1949).

[2] G. Waddington, J. C. Smith, D. W. Scott and H. M. Huffman, THIS JOURNAL, **71**, 3902 (1949).

[3] (a) G. Waddington, S. S. Todd and H. M. Huffman, *ibid.*, **69**, 22 (1947); G. Waddington and D. R. Douslin, *ibid.*, **69**, 2275 (1947).

[4] S. C. Schuman, J. G. Aston and M. Sagenkahn, *ibid.*, **64**, 1039 (1942).

[5] American Petroleum Institute Research Project 44, Selected Values of Properties of Hydrocarbons, Table 1 k, June 30, 1944.

Table I

Vapor Heat Capacity of 2-Methylbutane in Cal./Deg./Mole

T, °K.	317.20	358.15	402.30	449.20	487.05
C_p (760 mm.)	30.650	33.580	36.890	40.335	42.995
C_p (338 mm.)	30.260	33.395	36.798	40.280	42.955
C_p^0	29.95	33.25	36.72	40.24	42.93
$(\partial C_p/\partial P)_T$ (obs.)	0.70	0.33	0.17	0.10	0.07
$(\partial C_p/\partial P)_T$ (calcd.)	0.70	0.34	0.17	0.10	0.07

where V_L is the molar volume of the liquid. In addition, the values of C_p as a function of pressure at five temperatures 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 the empirical equation

$$B = -577 - 12.01e^{1150/T} \text{ cc./mole} \qquad (4)$$

The method of evaluating the constants in this equation has been described elsewhere.[6] The values of the second virial coefficient calculated from the observed heats of vaporization at 279.48, 298.16 and 301.01°K. are −1313, −1155 and −1114 cc./mole; the values given by equation (4) for these same temperatures are −1313, −1149 and −1126 cc./mole. The observed values of $(\partial C_p/\partial P)_T$ are compared with those given by equation (4) in the last two lines of Table I.

Entropy.—The entropy of 2-methylbutane vapor was computed at the three temperatures at which the heat of vaporization was measured. These calculations are summarized in Table II. The entropy of the liquid is from the work of Guthrie and Huffman,[7] and the compression term utilizes the vapor pressure equation of reference 5. For computing the gas imperfection term, which is given by $P(\partial B/\partial T)_P$ in terms of the second virial coefficient, equation (4) was used.

Table II

Entropy of 2-Methylbutane Vapor in Cal./Deg./Mole

T, °K.	279.48	298.16	301.01
S^0, liq.	59.74	62.24	62.62
Vaporization, $\Delta H_{\text{vap.}}/T$	22.12	19.91	19.60
Compression, R ln $(P/760)$	−1.61	−0.20	0.00
Gas imperfection	0.12	0.16	0.17
S^0, gas	80.37	82.11	82.39

Discussion

Vibrational Assignments.—Before discussing the calorimetric data for 2-methylbutane and 2,3-dimethylbutane in relation to the energy differences between the rotational isomers, it is necessary to have adequate vibrational assignments for both molecules. The Raman and infrared spectra of these compounds have been studied by several investigators.[8-11] Table III lists the observed Raman lines and infrared bands below 1,500 cm.$^{-1}$ In anticipation of the results of a subsequent section, these spectroscopic data will be interpreted in terms of the molecular structures which were found to be consistent with the thermal data. In the case of 2-methylbutane, only the stable rotational isomer of C_1 symmetry is present in appreciable concentrations at and below room temperature, and all of the observed frequencies were assigned to this one form. In the case of 2,3-dimethylbutane, on the other hand, both rotational isomers are present in significant concentrations, and it was neces-

Table III

Raman, cm.$^{-1}$	Infrared, cm.$^{-1}$
2-Methylbutane	
165 w	
246 w	
367 w	
415 w	
465 s	463 w
	534 w
764 s	765 vs
	779 vw
795 s	796 s
907 m	912 s
	920 s
950 w	
	978 s
1016 w	1022 s
1036 m	1043 m
1101 w	
	1135 vw
1144 w	1154 vs
1168 m	1176 s
1270 vw	1276 m
1295 w	1302 m
1335 m	1335 m
	1352 m
	1366 vs
	1387 vs
1454 vs	1467 vs
2,3-Dimethylbutane	
292 w	
346 w	
382 w	
427 w	
478 m	480 w
2,3-Dimethylbutane (cont.)	
503 m	
	541 m
605 vw	
657 vw	
729 vs	729 m
755 s	
812 w	
	832 w
869 m	870 s
	910 s
	921 s
932 s	
942 s	
956 s	956 w
	991 s
	1028 s
1035 m	1038 vs
	1066 s
	1083 vw
	1106 w
	1129 vs
1151 m	1153 vs
1163 m	
1198 m	1196 w
1239 vw	
	1280 s
1302 m	1297 m
	1308 w
1326 vw	
1346 m	
	1372 vs
1383? w	1382 vs
1446 vs	
1468 vs	1462 vs

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[6] D. W. Scott, G. Waddington, J. C. Smith and H. M. Huffman, *J. Chem. Phys.*, **15**, 565 (1947).

[7] G. B. Guthrie and H. M. Huffman, This Journal, **65**, 1139 (1943).

[8] Raman for 2-methylbutane: (a) J. Weiler, *Z. Physik*, **69**, 586 (1931); (b) H. Kopper, R. Seka and K. W. F. Kohlrausch, *Sitzber. Akad. Wiss. Wien, Math-naturw. Klasse. Abt. IIa*, **141**, 465 (1932); (c) L. Kahovec and J. Wagner, *Z. physik. Chem.*, **B47**, 48 (1940); (d) P. A. Bazhulin, A. F. Plate, O. P. Solovova and B. A. Kazanskii, *Bull. acad. sci. U. R. S. S., Classe sci. chim.*, 13 (1941); (e) M. R. Fenske, W. G. Braun, R. V. Wiegand, Dorothy Quiggle, R. H. McCormick and D. H. Rank, *Anal. Chem.*, **19**, 700 (1947).

[9] Infrared for 2-methylbutane: (a) P. Lambert and J. Lecomte, *Compt. rend.*, **206**, 1174 (1938); *Ann. phys.*, **10**, 503 (1938); (b) American Petroleum Institute Research Project 44 at the National Bureau of Standards, Catalog of Infrared Spectrograms, Serial No's. 64 (gas), 241, 441 (gas), 550, 555 and 783, (c) R. S. Rasmussen, *J. Chem. Phys.*, **16**, 712 (1948) (gas); (d) D. W. E. Axford and D. H. Rank, *ibid.*, **18**, 51 (1950) (solid and liquid at −80°).

[10] Raman for 2,3-dimethylbutane: (a) A. Andant, P. Lambert and J. Lecomte, *Compt. rend.*, **198**, 1316 (1934); (b) E. J. Rosenbaum, A. V. Grosse and H. F. Jacobson, This Journal, **61**, 689 (1939); (c) P. A. Bazhulin, M. F. Bokshteĭn, A. L. Liberman, M. Yu. Lukina, E. I. Margolis, O. P. Solovova and B. A. Kazanskii, *Bull. acad. sci. U. R. S. S., Classe sci. chim.*, 198 (1943); (d) ref. 8e.

[11] Infrared for 2,3-dimethylbutane: (a) P. Lambert and J. Lecomte, *Ann. phys.*, **18**, 329 (1932); (b) C. F. Kettering and W. W. Sleator, *Physics*, **4**, 39 (1933) (gas); (c) ref. 9a; (d) ref. 9b, Serial No's. 246, 656, 670, 789, 810 and 811; (c) ref. 9d (solid and liquid at −80°).

sary to sort out the frequencies associated with each of them.

As the correct assignment of the skeletal bending frequencies was particularly important in this work, approximate normal coördinate calculations were used as a guide in assigning them. For calculating these bending frequencies, the problems were simplified to those of five- and six-atom molecules by substituting masses of 15.034, 14.026 and 13.018 for the CH_3, CH_2 and CH groups, respectively, and were further simplified by factoring out the C–C stretching vibrations by Wilson's method.[12] The latter simplification was equivalent to setting the force constants for C–C stretching equal to infinity. The force constants for C–C–C angle bending were selected to give exact agreement with the skeletal bending frequencies of 2-methylpropane and propane, and with the totally symmetric skeletal bending frequencies of the C_{2h} and C_2 forms of *n*-butane, when these four molecules were treated in the same way as 2-methylbutane and 2,3-dimethylbutane. These force constants, in ergs/radian^2, are: for a C–C–C angle whose vertex is a CH group, 0.921×10^{-11}; for the interaction between two such angles with a side and vertex in common, 0.142×10^{-11}; for a C–C–C angle whose vertex is a CH_2 group, 0.805×10^{-11}; for the interaction between two C–C–C angles having only a side in common, 0.177×10^{-11} when the two C–C–C planes are coplanar as in the C_{2h} form of *n*-butane and 0.210×10^{-11} when the dihedral angle between the two C–C–C planes is 60°, as in the C_2 form of *n*-butane. Interactions between two C–C–C angles having no side in common were neglected. Table IV lists the calculated frequencies and gives the assignment of the observed frequencies made with the aid of the calculated values. Some frequencies of 2,3-dimethylbutane that have not been observed directly were assigned by interpreting weak Raman lines as allowed overtones or sum-combinations.

TABLE IV

SKELETAL BENDING FREQUENCIES, CM.$^{-1}$

		Calcd.	Obsd.		Overtone or comb.
			Raman	Infrared	
2-Methylbutane C_1 symmetry		231	246		
	A	359	367		
	R, IR	387	415		
		464	465	463	
2,3-Dimethylbutane, C_2 symmetry		243	292		
	A	341	382		
	R, IR	468	478	480	
	B	215			230[a]
	R, IR	364	427		
		476	478	480	
2,3-Dimethylbutane, C_{2h} symmetry	A_g	314	346		
	R	529	503		
	B_u	283			303[b]
	IR	391			406[c]
	B_g, R	409			469[d]
	A_u, IR	204			

[a] $230 + 427 = 657(A)$. [b] $2 \times 303 = 606(A_g)$. [c] $2 \times 406 = 812(A_g)$. [d] See discussion in text.

The vibrational assignment for 2-methylbutane was readily made by using the knowledge obtained from simpler related molecules as to the regions of the spectrum in which the frequencies of particular types of vibrations are expected to occur. As is usual in molecules of this complexity, the thermodynamically unimportant methyl bending, methylene bending and C–H stretching frequencies are not all resolved in the spectra, and it was necessary to use average or conventional values for these modes. The assignment for 2-methylbutane is as follows: skeletal bending, 246, 367, 415 and 464; CH_2 rocking, 765; C–C stretching, 795, 978, 1150 and 1175; CH_3 rocking, 910, 920, 950, 1020, 1040 and 1100; CH_2 wagging, 1275; CH_2 twisting, 1300; C–H wagging, 1335 and 1350; CH_3 and CH_2 bending, 1375 (3) and 1465 (7); and C–H stretching, 2950 (12) cm.$^{-1}$. The weak Raman line at 165 cm.$^{-1}$ is ascribed to skeletal torsion; the weak infrared bands at 534, 779 and 1135 cm.$^{-1}$ are interpreted as the combinations $165 + 367 = 532$, $367 + 415 = 782$ and $367 + 765 = 1132$.

It is necessary to make a complete vibrational assignment for only one of the rotational isomers of 2,3-dimethylbutane, provided that the moments of inertia for over-all and internal rotation are computed for this same configuration. This is true because changes in vibrational frequencies resulting from internal rotation approximately compensate for the corresponding changes in the moments of inertia in the complete partition function.[13] The assignment was made for the isomer of C_2 symmetry, because the concentration of this form is twice that of the other isomer, and because the less stringent selection rules for the C_2 form permit all frequencies to appear in both spectra. As the hydrogen vibrations of rotational isomers seldom differ enough to be resolved in the spectrum, the only frequencies of the C_{2h} form that need to be identified, in addition to those for skeletal bending that have already been considered, are those for C–C stretching. The frequencies that appear only in the Raman spectrum at 755 and 1163 cm.$^{-1}$ are assigned to one of the A_g modes and to the B_g mode of the C_{2h} form. The doublet, 932–942 cm.$^{-1}$, in the Raman spectrum is attributed to Fermi resonance between the other A_g mode and the overtone of the B_g skeletal bending mode. This places the latter at about 469 cm.$^{-1}$, where it would be obscured in the Raman spectrum because of its proximity to a strong line of the other isomer. The doublet, 910–921 cm.$^{-1}$, in the infrared spectrum is attributed to Fermi resonance between the B_u mode and the combination $406 + 503 = 909$ (B_u). The A_u mode either does not appear in the infrared spectrum or else coincides with a band of the other isomer.

All the observed frequencies not identified with the skeletal modes of the C_{2h} form are used for the C_2 form. As in the case of 2-methylbutane, average or conventional values must be used for the frequencies above 1350 cm.$^{-1}$. The assignment for the C_2 form of 2,3-dimethylbutane is: skeletal bending, 230, 292, 382, 427 and 480 (2); C–C stretching, 730, 870, 955 and 1195 (2); CH_3 rocking, 990, 1030, 1040, 1065, 1085, 1105, 1130 and 1150; C–H wagging, 1280, 1300, 1325 and 1345; CH_3 bending, 1375 (4) and 1465 (8); C–H stretch-

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(12) E. B. Wilson, Jr., *J. Chem. Phys.*, **9**, 76 (1941).

(13) K. S. Pitzer, *J. Chem. Phys.*, **14**, 239 (1946).

ing, 2950 (14) cm.$^{-1}$. Three weak Raman lines have already been interpreted as overtones or combinations (footnotes of Table IV). The infrared band at 541 cm.$^{-1}$ and the one at 832 cm.$^{-1}$ which appears only at low temperatures are not readily explained in terms of the assigned fundamental frequencies; these may be combination bands involving the unobserved skeletal torsional frequency. Because of the complexities inherent in separating the frequencies of two rotational isomers, and because the lowest skeletal bending frequency was obtained from a sum-combination and was not observed directly, the assignment for 2,3-dimethylbutane is necessarily less reliable than that for 2-methylbutane.

Moments of Inertia.—As both 2-methylbutane and 2,3-dimethylbutane are cases of compound rotation, they were treated by the methods of Kilpatrick and Pitzer.[14] A C–C distance of 1.54 Å., a C–H distance of 1.09 Å. and tetrahedral bond angles were used throughout. For the C_1 form of 2-methylbutane, the ethyl group was taken to be rotated 130° 21′ from its position in the C_s form; for the C_2 form of 2,3-dimethylbutane, an isopropyl group was taken to be rotated exactly 120° from its position in the C_{2h} form. These configurations correspond to the minima in the potential functions for skeletal rotation, which will be discussed in the next section. The products of the three principal moments of inertia were calculated to be $8{,}920 \times 10^{-117}$ g.^{3} cm.^{6} for 2-methylbutane and $21{,}240 \times 10^{-117}$ g.^{3} cm.^{6} for 2,3-dimethylbutane. The off-diagonal elements are small in the reduced internal rotational matrix (D) of each of these molecules. Neglecting these off-diagonal elements affects the square root of the determinant of D by 2.1% for 2-methylbutane and by 1.0% for 2,3-dimethylbutane. Therefore, it is justifiable to use the diagonal elements as reduced moments of inertia. For 2-methylbutane these are 28.03×10^{-40} g. cm.^{2} for skeletal rotation, 5.097×10^{-40} g. cm.^{2} for the methyl rotation of the ethyl group, and 5.099×10^{-40} and 5.189×10^{-40} g. cm.^{2} for the methyl rotations of the isopropyl group. For 2,3-dimethylbutane the reduced moments are 55.12×10^{-40} g. cm.^{2} for skeletal rotation, 5.219×10^{-40} g. cm.^{2} for two of the methyl rotations and 5.180×10^{-40} g. cm.^{2} for the other two.

Barriers to Internal Rotation.—For the methyl rotations of 2-methylbutane, independent threefold cosine-type barriers were assumed. When an attempt was made to fit the calorimetric entropy and heat capacity data, assuming a threefold cosine-type barrier for the skeletal rotation as well, it was found that a fit could not be obtained without using quite unreasonable values for the heights of the barriers hindering the methyl rotations. This is convincing evidence that the rotational isomers of 2-methylbutane do not have the same energy. For purposes of thermodynamic calculations, the procedure adopted was to transfer barrier heights for methyl rotations from simpler related molecules and then use the calorimetric data to evaluate the two parameters of an unsymmetrical barrier for the skeletal rotation. The barrier heights taken for the methyl rotations were 3400 cal./mole as in propane[15] for the methyl rotation of the ethyl group, and 3620 cal./mole as in 2-methylpropane[16] for the methyl rotations of the isopropyl group. This transfer of barrier heights for the methyl rotations is probably a good approximation; in the C_1 configuration of 2-methylbutane it is unlikely that there is any serious steric repulsion between the methyl group on the ethyl group and the nearest one on the isopropyl group, because the ethyl group can rotate to relieve such repulsion.

Of several unsymmetrical barriers for the skeletal rotation of 2-methylbutane that were tried, the following was found to give satisfactory agreement with the calorimetric values of the entropy and heat capacity and was used for subsequent thermodynamic calculations

$$V = {}^1/_2(1860)(1 - \cos 3\phi) + {}^1/_4(10{,}700)(1 + \cos \phi)^2 - 466 \text{ cal./mole} \quad (5)$$

Here ϕ is the angle of skeletal rotation measured from the C_s configuration.

For the methyl rotations of 2,3-dimethylbutane, independent, threefold, cosine-type potential barriers were assumed as before. For this molecule it would not be valid to transfer barrier heights from a simpler molecule such as 2-methylpropane, because the methyl groups in 2,3-dimethylbutane are so arranged that in either equilibrium position there are probably large steric repulsions between them that are not present in the simpler molecule. It was found that a fit could be obtained with the calorimetric entropy and heat capacity data of 2,3-dimethylbutane assuming a threefold, cosine-type barrier for the skeletal rotation and using a reasonable value for the height of the barriers hindering the methyl rotations. This is evidence that the rotational isomers of 2,3-dimethylbutane have the same or nearly the same energy. The values of the barrier heights that were used for thermodynamic calculations were 2060 cal./mole for the skeletal rotation and 4100 cal./mole for each of the four methyl rotations. Strictly, in the C_2 configuration there are two non-equivalent pairs of potential barriers for methyl rotation, but the difference between them is probably small, and for thermodynamic purposes it is satisfactory to use the single average value for the barrier height given above.[16a]

Thermodynamic Functions.—The vibrational frequencies, moments and reduced moments of inertia and potential barriers hindering internal rotation given in previous sections were used to

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(14) J. E. Kilpatrick and K. S. Pitzer, *J. Chem. Phys.*, **17**, 1064 (1949).

(15) K. S. Pitzer, *ibid.*, **12**, 310 (1944).

(16) K. S. Pitzer and J. E. Kilpatrick, *Chem. Revs.*, **39**, 435 (1946).

(16a) Note Added in Proof.—Since the submission of this paper, F. F. Cleveland and P. Porcelli [*J. Chem. Phys.*, **18**, 1459 (1950)] have reported additional Raman data for 2,3-dimethylbutane which necessitate a minor revision of the vibrational assignment for that molecule. The Raman displacement at 271 cm.$^{-1}$ observed by these investigators is assigned to the lowest skeletal bending frequency of the C_2 form for which the value 230 cm.$^{-1}$ was used previously. The infrared band at 541 cm.$^{-1}$ and the weak Raman line at 657 cm.$^{-1}$ are now interpreted as 2 × 271 (A) and 271 + 382 (B), respectively. With this revised assignment, the barrier heights required to fit the calorimetric data are 2000 cal./mole for the skeletal rotation and 3900 cal./mole for each of the methyl rotations. The calculated thermodynamic functions for 2,3-dimethylbutane in Tables V and VI have been revised in proof to be consistent with the newer vibrational assignment and values of the barrier heights.

compute thermodynamic functions for 2-methylbutane and 2,3-dimethylbutane. Values of the physical constants given by Wagman, *et al.*,[17] were used. The reduced moment of inertia for the skeletal rotation of 2-methylbutane was large enough to permit that motion to be treated classically. For computing the contributions of skeletal rotation to the thermodynamic functions, the classical partition function and its first and second derivatives with respect to temperatures were integrated numerically. Simpson's rule was used with 10° intervals of ϕ.

A comparison of the calorimetric and calculated values of the entropy and vapor heat capacity is given in Table V. The differences between the observed and calculated values of the heat capacity at the higher temperatures are no greater than is to be expected from the neglect of anharmonicity in computing the latter.[17a]

TABLE V

2-Methylbutane			2,3-Dimethylbutane		
Entropy, cal./deg./mole			Entropy, cal./deg./mole		
T, °K.	Obsd.	Calcd.	T, °K.	Obsd.[a]	Calcd.
279.48	80.37	80.37	298.16	87.43	87.42
298.16	82.11	82.12	313.13	89.12	89.10
301.01	82.39	82.39	331.15	91.09	91.10
C_p^0, cal./deg./mole			C_p^0, cal./deg./mole		
T, °K.	Obsd.	Calcd.	T, °K.	Obsd.[a]	Calcd.
317.20	29.95	29.93	341.60	37.78	37.76
358.15	33.25	33.22	371.20	40.69	40.60
402.30	36.72	36.66	402.30	43.63	43.52
449.20	40.24	40.18	436.00	46.73	46.62
487.05	42.93	42.83	471.15	49.77	49.63

[a] Ref. 2.

Table VI lists values of the functions $(H_0^0 - F_T^0)/T$, $H_T^0 - H_0^0$, S^0, and C_p^0 for selected temperatures up to 1500°K. Most of the entries in the table are given to more decimal places than is justified by their absolute accuracy in order to retain internal consistency among the several functions.

TABLE VI

T, °K.	$(H_0^0 - F_T^0)/T$, cal./deg./mole	$H_T^0 - H_0^0$, kcal./mole	S^0, cal./deg./mole	C_p^0, cal./deg./mole
		2-Methylbutane		
298.16	64.36	5.295	82.12	28.39
300	64.47	5.346	82.29	28.54
400	70.07	8.596	91.56	36.49
500	75.28	12.62	100.51	43.71
600	80.21	17.30	109.05	49.89
700	84.92	22.57	117.17	55.19
800	89.44	28.30	124.82	59.71
900	93.77	34.49	132.09	63.66
1000	97.96	41.01	138.97	67.12
1100	101.98	47.88	145.51	70.10
1200	105.87	55.03	151.73	72.68
1300	109.65	62.39	157.64	74.93
1400	113.28	69.99	163.27	76.88
1500	116.78	77.74	168.61	78.55
		2,3-Dimethylbutane		
298.16	67.58	5.916	87.42	33.59
300	67.70	5.978	87.63	33.76
400	74.06	9.833	98.64	43.30
500	80.05	14.61	109.26	51.94
600	85.77	20.17	119.38	59.23
700	91.27	26.41	129.00	65.41
800	96.54	33.23	138.07	70.67
900	101.67	40.50	146.67	75.19
1000	106.57	48.24	154.80	79.13
1100	111.33	56.30	162.51	82.53
1200	115.88	64.77	169.81	85.49
1300	120.29	73.41	176.76	88.06
1400	124.57	82.31	183.36	90.31
1500	128.70	91.40	189.64	92.25

Energy Differences between Rotational Isomers.—The potential energy function used for the skeletal rotation of 2-methylbutane, eq. (5), has no minimum at the C_s configuration but, instead, has a broad maximum 10.2 kcal./mole higher than the minima corresponding to the C_1 configurations. Because of the arbitrary nature of this assumed potential function and the uncertainties inherent in thermodynamic calculations for a molecule of this complexity, little quantitative significance can be attached to the detailed shape of this potential function. Qualitatively, however, it is evident that the C_s configuration is less stable than the C_1 form by at least several thousand calories per mole.

The use of a simple threefold barrier for skeletal rotation in 2,3-dimethylbutane implies a zero energy difference between the rotational isomers of that molecule. The complexity of the statistical calculations makes it impractical to set limits of uncertainty to this value. However, having the evidence from the thermal data that the energy difference is very small, one may utilize the spectroscopic results of Szasz and Sheppard[1] to set an upper limit of about 100 cal./mole for this difference.

Thomas and Gwinn[18] have studied the energy differences between the rotational isomers of 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane by dipole moment measurements. These compounds differ from those studied in this investigation in the replacement of methyl groups with chlorine atoms. Thomas and Gwinn found that the C_s form of 1,1,2-trichloroethane is at least 4000 cal./mole less stable than the C_1 form and that the energy difference be-

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(17) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

(17a) NOTE ADDED IN PROOF.—It has been suggested (ref. 1) that the low-temperature crystalline form of 2,3-dimethylbutane may be a solid solution of the rotational isomers, in which case a residual entropy of $R \ln 3$ would be retained at temperatures approaching the absolute zero. It is possible to fit the calorimetric vapor heat capacity at 340°K. and an entropy at 298.16°K. that is $R \ln 3$ greater than the calorimetric value by using barrier heights of 2600 cal./mole for the methyl rotations and 1700 cal./mole for the skeletal rotation. However the calculated value of the vapor heat capacity is then nearly three per cent. lower than the observed value at 470°K. Furthermore, barrier heights of 2600 cal./mole for the methyl rotations seem unreasonably low in view of the fact that such branched hydrocarbons as 2-methylpropane, 2,2-dimethylpropane, and 2,2-dimethylbutane have barrier heights for methyl rotation greater than 3500 cal./mole. Since the assumption that the calorimetric value of the entropy is correct results in agreement of the observed and calculated values of the vapor heat capacity over a wide range of temperature, it seems unlikely that residual entropy is retained at low temperatures. The observation of the vibrational frequencies of both rotational isomers in the spectra of the solid seems to indicate that the low-temperature crystalline form is an ordered arrangement of the rotational isomers' An alternative but less likely interpretation would be that the spectroscopic observations were made on the supercooled liquid (glass) or on the crystalline form stable above 136°K. in a supercooled condition.

(18) J. R. Thomas and W. D. Gwinn, THIS JOURNAL, **71**, 2785 (1949).

tween the two forms of 1,1,2,2-tetrachloroethane is less than 200 cal./mole. The parallelism between these two compounds and 2-methylbutane and 2,3-dimethylbutane is striking. Thomas and Gwinn's discussion of the energy differences between the rotational isomers of the chlorine compounds in terms of steric repulsions and distortions of bond angles from tetrahedral values applies equally well to the methyl compounds studied in this work. The similar results for the polar and relatively non-polar pairs of compounds supports the idea that bond dipole interactions are unimportant in determining configurational stability.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CATHOLIC UNIVERSITY OF AMERICA]

Substituent Effects in the Acid and Base Hydrolyses of Aromatic Amides[1]

BY ISABEL MELOCHE AND KEITH J. LAIDLER

A kinetic study has been made of the acid and base hydrolyses of benzamide, *p*-nitrobenzamide, *p*-chlorobenzamide, *p*-methylbenzamide and *o*-methylbenzamide. Activation energies, frequency factors and entropies of activation have been obtained. The changes in rate are found to be influenced mainly by changes in activation energy, but in both series ΔS^* increases approximately linearly with E. It is found that in alkaline hydrolysis electron-attracting groups lower E, while electron-repelling groups raise it; in acid solution electron-attracting groups raise E and electron-repelling ones lower it. A mechanism is proposed which explains the substituent effect and also the different effects observed in the acid and base hydrolyses of esters and the acid hydrolysis of anilides.

Introduction

In contrast to the situation with the aromatic esters,[2,3] very little information has been available with respect to substituent effects on the acid and base hydrolyses of amides. Emmet Reid[4] made some studies of this type, in aqueous solution and at 100°, but it seems likely that at least in some cases he was measuring the rate of solution of the amide rather than that of its hydrolysis. Various studies of the catalysis of aliphatic amides have been made,[5] and Karve and Kelkar[6] have recently investigated the kinetics of the acid hydrolysis of a number of substituted anilides.

In the present paper are reported kinetic data for the acid and base hydrolysis, in a 60-40 (by volume) alcohol–water mixture, of benzamide and four substituted benzamides.

Experimental

The amides used were benzamide, *p*-nitrobenzamide, *p*-chlorobenzamide, *p*-methylbenzamide (*p*-toluamide) and *o*-methylbenzamide (*o*-toluamide). All were obtained commercially except the *p*-chloro compound, which was prepared from the acid chloride. The amides were tested for purity by melting point determinations and were recrystallized when necessary.

The compounds are not sufficiently soluble in water, even at high temperature, to allow a reasonable concentration to be obtained. The 60-40 ethyl alcohol–water mixture was found to be suitable in all cases. Both the amide and the acid or base were put into solution at concentrations of 0.05 *M*, and as equal amounts (5 cc.) were mixed together in the reaction tubes the final concentration of each was 0.025 *M*. For the alkali sodium hydroxide was used; for the acid, benzene sulfonic acid. The latter has been found to be completely dissociated at the concentrations used, but unlike the mineral acids it does not esterify the alcohol present.[3]

The reactions were carried out in sealed tubes maintained for various lengths of time in thermostatically controlled oil-baths. Pyrex glass was used for the acid hydrolysis, but was unsuitable for the alkaline hydrolysis, being seriously etched, with marked removal of hydroxyl ions, at the higher temperatures used (80 and 100°). Corning brand alkali-resistant glass, no. 728, was used and was found to be entirely satisfactory.

Runs were carried out at four temperatures except with the very slowly hydrolyzed *o*-toluamide, which was hydrolyzed at three temperatures only with both acid and base. Tubes were removed after various periods of time and analyzed colorimetrically for ammonia after Nesslerization. It was established by separate experiments that the reaction gave mainly the acid and only to a negligible extent the ethyl ester.

Results

In all cases the second-order law was found to be obeyed accurately, constants being calculated using the equation $k = x/ta(a - x)$. Activation energies and frequency factors were obtained from the variation of log k with $1/T$, the method of least squares being used in all cases. The entropy of activation, ΔS^*, was calculated from the frequency factor A by means of the equation[7]

$$A = e(kT/h)e^{\Delta S^*/R} \qquad (1)$$

The rate constants obtained at the temperatures used are collected in Table I, while the values of E, A and ΔS^* are given in Table II. Some typical Arrhenius plots are shown in Fig. 1.

The least square treatment of the data indicates that the probable error in the activation energies is in all cases ±0.15 to ±0.20 kcal., and that the probable error in the entropies of activation is 0.4 to 0.55 entropy unit. In view of this the variation of ΔS^* with E, to be discussed in the next section, is entirely significant with respect to the experimental uncertainty.

Discussion

General.—It is to be noted from Table I that (except with the ortho compound) the alkaline

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(1) Abstracted from a dissertation submitted by Sister Isabel of Carmel Meloche, S.H.M., to the faculty of the Graduate School of Arts and Sciences of the Catholic University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) C. K. Ingold and W. J. Nathan, *J. Chem. Soc.*, 222 (1936).

(3) E. W. Timm and C. N. Hinshelwood, *ibid.*, 862 (1938).

(4) E. Emmet Reid, *Am. Chem. J.*, **21**, 284 (1899); **24**, 397 (1900).

(5) J. C. Crocker, *J. Chem. Soc.*, **91**, 593 (1907); J. C. Crocker and F. H. Lowe, *ibid.*, **91**, 952 (1907); S. F. Acree and S. Nirdlinger, *Am. Chem. J.*, **38**, 489 (1907); W. J. Taylor, *J. Chem. Soc.*, 2741 (1930); V. K. Krieble and K. A. Holst, THIS JOURNAL, **60**, 2976 (1938); B. S. Rabinovitch and C. A. Winkler, *Can. J. Research*, **B20**, 73 (1942).

(6) D. D. Karve and B. W. Kelkar, *Proc. Indian Acad. Sci.*, **24**, 254 (1946).

(7) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 417.