[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BROOKLYN COLLEGE]

Correlation of Heats of Isomerization, and Differences in Heats of Vaporization of Isomers, Among the Paraffin Hydrocarbons

BY HARRY WIENER

The paraffin hydrocarbons, formerly considered to be inert at ordinary temperatures, have in recent years been found to participate in many catalytic reactions of importance in the petroleum industry. To facilitate the exploration and development of new reactions, and to aid in the determination of conditions of highest yield and economy, extensive and complete tabulations of thermochemical properties characteristic of the compounds involved are necessary. A method of correlation of such properties is of value in summarizing the available data, in checking its consistency, as well as in permitting the prediction of thermochemical properties for compounds for which experimental observations are not yet available.

A method for the calculation of boiling points, described in a previous paper,[1] has been found to be applicable to the prediction of the heats of isomerization and the differences in heats of vaporization of the isomeric paraffins liquid at 25°.

The heat of isomerization, ΔH_i, represents the increment in heat content, in kcal./mole, for the reaction: $n\text{-}C_nH_{2n+2}(\text{liq}) \rightarrow \text{iso-}C_nH_{2n+2}(\text{liq}) - \Delta H_i$, at 25° and constant pressure. The estimated uncertainty of the experimental data is 0.2–0.4 kcal./mole.

The heat of vaporization, ΔH_v, represents the increment in heat content, in kcal./mole, for the process: $C_nH_{2n+2}(\text{liq}) \rightarrow C_nH_{2n+2}\ (\text{g}) - \Delta H_v$, at saturation pressure and 25°. Estimated average uncertainty 0.01–0.05 kcal./mole.

The reference values for the normal paraffins are given in Table I.[2]

TABLE I

REFERENCE VALUES FOR THE NORMAL PARAFFINS

Cpd.	w_0	p_0	Heat of combustion $-\Delta H_{c_n}$	Heat of formation ΔH_{f_n}	Heat of vaporization ΔH_{v_n}
n-Pentane	20	2	838.8	−41.4	6.32
n-Hexane	35	3	995.0	−47.5	7.54
n-Heptane	56	4	1151.3	−53.6	8.74
n-Octane	84	5	1307.5	−59.7	9.92
n-Nonane	120	6	1463.8	−65.8	11.10
n-Decane	165	7	1620.1	−72.0	12.28

The data for the heats of combustion, formation and vaporization were taken from the selected best values of these properties for the 33 paraffins up to C_8H_{18} which normally are liquid at 25°, in the tables of the American Petroleum Institute Research Project 44.[3] These values, in the main, summarize previously published work[4,5,6] by Rossini and his associates at the National Bureau of Standards. No published data for the branched-chain paraffins above the octanes are available.

Method of Calculation

The polarity number p is defined as the number of pairs of carbon atoms which are separated by three carbon–carbon bonds.

TABLE II

C_5H_{12}	Δw	Δp	$-\Delta H_i$ obs.	$-\Delta H_i$ calcd.	$\Delta H_{v_n} - \Delta H_v$ obs.	$\Delta H_{v_n} - \Delta H_v$ calcd.
n-Pentane	0	0	0.0	0.0	0.00	0.00
2-Methylbutane	2	0	1.5	1.2	.44	.41
C_6H_{14}						
n-Hexane	0	0	0.0	0.0	.00	.00
2-Methylpentane	3	0	1.3	1.3	.40	.41
3-Methylpentane	4	−1	0.7	0.6	.31	.33
2,2-Dimethylbutane	7	0	3.5	3.0	.92	.96
2,3-Dimethylbutane	6	−1	2.0	1.5	.58	.60
C_7H_{16}						
n-Heptane	0	0	0.0	0.0	.00	.00
2-Methylhexane	4	0	1.3	1.3	.42	.41
3-Methylhexane	6	−1	0.7	0.8	.35	.40
3-Ethylpentane	8	−2	.1	.3	.32	.38
2,2-Dimethylpentane	10	0	3.4	3.2	.98	1.00
2,3-Dimethylpentane	10	−2	2.2	1.0	.55	0.59
2,4-Dimethylpentane	8	0	2.5	2.5	.87	.82
3,3-Dimethylpentane	12	−2	2.4	1.6	.84	.80
2,2,3-Trimethylbutane	14	−2	3.0	2.2	1.08	1.00
C_8H_{18}						
n-Octane	0	0	0.0	0.0	0.00	.00
2-Methylheptane	5	0	1.2	1.2	.43	.41
3-Methylheptane	8	−1	0.6	0.8	.40	.44
4-Methylheptane	9	−1	.4	1.0	.43	.52
3-Ethylhexane	12	−2	.2	0.7	.44	.55
2,2-Dimethylhexane	13	0	2.9	3.1	1.00	1.07
2,3-Dimethylhexane	14	−2	0.7	1.2	0.64	0.71
2,4-Dimethylhexane	13	−1	1.7	2.0	.89	.85
2,5-Dimethylhexane	10	0	2.5	2.4	.87	.83
3,3-Dimethylhexane	17	−2	1.9	1.9	.94	.96
3,4-Dimethylhexane	16	−3	0.5	0.6	.60	.66
2-Methyl-3-ethylpentane	17	−3	.0	.8	.71	.74
3-Methyl-3-ethylpentane	20	−4	.7	.5	.83	.77
2,2,3-Trimethylpentane	21	−3	1.7	1.8	1.09	1.07
2,2,4-Trimethylpentane	18	0	2.2	4.3	1.52	1.48
2,3,3-Trimethylpentane	22	−4	0.9	0.9	1.02	0.93
2,3,4-Trimethylpentane	19	−3	1.3	1.3	0.90	.90

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(1) Wiener, THIS JOURNAL, **69**, 17 (1947).

(2) The heats of combustion and of formation of the isomeric paraffins may be calculated by combining the reference values in table I with the calculated values of the heat of isomerization.

(3) American Petroleum Institute Research Project 44 at the National Bureau of Standards, Selected Values of Properties of Hydrocarbons. Tables 1m, 2m, 3m, 1n, 2n, 3n, 1p, 2p, 3p, dated March 31, 1944, and April 30, 1945.

(4) Rossini, *Chem. Rev.*, **27**, 1 (1940).

(5) Knowlton and Rossini, *J. Research Bur. Standards*, **23**, 415 (1939).

(6) Prosen and Rossini, *ibid.*, **27**, 289 (1941); **27**, 519 (1941); **33**, 255 (1944); **34**, 163 (1945).

The path number w is obtained by multiplying the number of carbon atoms on one side of any bond by those on the other side and adding these values for all bonds; it is identical with the sum of the distances between the $[n(n-1)]/2$ pairs of carbon atoms in the molecule, and therefore is an inverse measure of compactness of the isomer.

The differences in the values of these variables for the normal and branched paraffins are expressed by the symbols Δw and Δp

$$\Delta w = w_0 - w; \ \Delta p = p_0 - p \qquad (1)$$

where w_0 and p_0 are the values of the structural parameters for the corresponding normal paraffin (Table I).

The heats of isomerization and the differences in the heats of vaporization are then given by the equations

$$-\Delta H_i = 15.5 \frac{\Delta w}{n^2} + 1.1 \Delta p \qquad (2)$$

$$\Delta H_{v_n} - \Delta H_v = 0.412 \frac{\Delta w}{n-3} + 0.22 \Delta p \qquad (3)$$

In Table II, the values for $-\Delta H_i$ and $(\Delta H_{v_n} - \Delta H_v)$ calculated from these equations are compared with the observed values. The average deviations are ±0.31 kcal./mole for the heat of isomerization and ±0.038 kcal./mole for the heat of vaporization. These values are of the order of the estimated experimental uncertainties for these properties.

TABLE III

Compd.	Δw	Δp	$-\Delta H_i$	$\Delta H_{v_n} - \Delta H_v$
n-Nonane	0	0	0.0	0.00
2-Methyloctane	6	0	1.2	.41
3-Methyloctane	10	−1	0.8	.47
4-Methyloctane	12	−1	1.2	.61
3-Ethylheptane	16	−2	0.9	.66
4-Ethylheptane	18	−2	1.2	.80
2,2-Dimethylheptane	16	0	3.1	1.10
2,3-Dimethylheptane	18	−2	1.2	0.80
2,4-Dimethylheptane	18	−1	2.3	1.02
2,5-Dimethylheptane	16	−1	2.0	0.88
2,6-Dimethylheptane	12	0	2.3	.83
3,3-Dimethylheptane	22	−2	2.0	1.07
3,4-Dimethylheptane	22	−3	0.9	0.85
3,5-Dimethylheptane	20	−2	1.6	.93
4,4-Dimethylheptane	24	−2	2.4	1.21
2-Methyl-3-ethylhexane	24	−3	1.3	0.99
2-Methyl-4-ethylhexane	22	−2	2.0	1.07
3-Methyl-3-ethylhexane	28	−4	1.0	1.04
3-Methyl-4-ethylhexane	26	−4	0.6	0.90
2,2,3-Trimethylhexane	28	−3	2.1	1.26
2,2,4-Trimethylhexane	26	−1	3.9	1.57
2,2,5-Trimethylhexane	22	0	4.2	1.51
2,3,3-Trimethylhexane	30	−4	1.3	1.18
2,3,4-Trimethylhexane	28	−4	1.0	1.04
2,3,5-Trimethylhexane	24	−2	2.4	1.21
2,4,4-Trimethylhexane	28	−2	3.2	1.48
3,3,4-Trimethylhexane	32	−5	0.6	1.10
3,3-Diethylpentane	32	−6	−0.5	0.88
2,2-Dimethyl-3-ethylpentane	32	−4	1.7	1.32
2,3-Dimethyl-3-ethylpentane	34	−6	−0.1	1.02
2,4-Dimethyl-3-ethylpentane	30	−4	1.3	1.18
2,2,3,3-Tetramethylpentane	38	−6	0.7	1.29
2,2,3,4-Tetramethylpentane	34	−4	2.1	1.46
2,2,4,4-Tetramethylpentane	32	0	6.1	2.20
2,3,3,4-Tetramethylpentane	36	−6	0.3	1.16

Table III gives the values of the heats of isomerization and of vaporization of the 35 nonanes, calculated from equations (2) and (3).

Relation between the Boiling Point and the Heats of Isomerization and Vaporization

The boiling points of the paraffins have been shown[1] to obey the relation

$$\Delta t = 98 \frac{\Delta w}{n^2} + 5.5 \Delta p \qquad (4)$$

On multiplying this equation by 0.158 and subtracting it from equation (2), we obtain

$$-\Delta H_i = 0.16 \Delta t + 0.2 \Delta p \qquad (5)$$

A similar relation holds for the heat of vaporization

$$\Delta H_{v_n} - \Delta H_v = 0.05 \ \Delta t - 0.08 \Delta p \qquad (6)$$

The average deviations between observed data and values calculated by means of these equations are ±0.35 for the heat of isomerization and ±0.048 kcal./mole for the heat of vaporization.

Equation (6) constitutes a new addition to the list of relations between heat of vaporization and boiling point. The accuracy of equations (5) and (6) is especially remarkable in view of their simplicity.

Discussion

The applicability of the method described here to boiling points, as well as to properties involved in a chemical reaction and a change of state, respectively, serves to support the suggestion, made in the previous paper, that the variables w and p are parameters possessing definite theoretical significance in the description of the structure of isomeric molecules.

The procedures applied in this paper may be applied to other properties and to other classes of liquid organic compounds. Preliminary calculations indicate that this method is applicable to the following additional properties of the paraffin hydrocarbons: molecular volume, molal refraction, specific dispersion, pressure coefficient of the boiling point, and surface tension. Work on this subject is in progress.

Summary

A method for calculating the heats of isomerization and the heats of vaporization of all branched-chain paraffin hydrocarbons is described. The method expresses the difference in the value of the property between a given normal paraffin and its isomers as a linear function of two structural parameters.

The required empirical constants were evaluated from the data on the 33 liquid paraffins, C_6 to C_8. The average deviation of the calculated from the observed values for these paraffins is ±0.31

kcal./mole for the heat of isomerization and ±0.038 kcal./mole for the heat of vaporization.

The simplified equations

$$-\Delta H_i = 0.16\,\Delta t + 0.02\Delta p$$
$$\Delta H_{v_n} - \Delta H_v = 0.05\,\Delta t - 0.08\Delta p$$

relate the heats of combustion and of vaporization of the paraffins to their boiling points.

Predicted values of thermochemical properties for the 35 nonanes are given.

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An Electron Diffraction Investigation of Formic Acid Monomer

BY VERNER SCHOMAKER AND JOHN MICHAEL O'GORMAN[1]

In the course of an investigation of the structure of some simple esters,[1a] it was found in the case of methyl formate that no satisfactory theoretical intensity curves could be obtained without deviating considerably in the formate radical from the structure assigned to formic acid monomer by Karle and Brockway.[2] It seemed unlikely that replacement of the acid hydrogen atom by a methyl group would lead to any considerable change in the structure of the formate group. In the case of the ester the investigation of possible models could not be exhaustive, due to the large number of parameters, and the possibility existed that some overlooked model might have given a satisfactory theoretical intensity curve. These two considerations made it seem worthwhile to reinvestigate the structure of formic acid monomer.

The present study has confirmed our doubts as to the validity of the earlier investigation, and shows that formic acid monomer, actually in close agreement with the simple esters, has a carbon-oxygen double bond distance only a trifle greater than normal, a carbon–oxygen single bond distance considerably less than normal (presumably due to resonance), and an O—C=O bond angle only slightly less than the angle 125¼° of the classical tetrahedral model. It appears that Karle and Brockway misinterpreted their photographs and greatly overstated the reliability of their work; the possibility of an important discrepancy between the two sets of photographs may be ruled out of consideration inasmuch as the experimental procedures, although differing somewhat in the means employed for obtaining monomeric molecules of formic acid, both appear to be satisfactory.

Experimental

Formic acid is largely in the form of dimer at temperatures where its vapor pressure is suitable for use in the usual electron diffraction apparatus. In order to obtain a vapor which was essentially pure monomer, it was decided to heat the liquid sample outside the apparatus to about 50°, to give the proper pressure (*ca.* 300 mm.), and then to admit the vapor into the camera through a stopcock and a special nozzle separately heated to approximately 250°. This scheme is different from that adopted by Karle and Brockway[2] and has the advantages of simplicity and convenience and of not requiring that the substance under investigation be maintained in contact with stopcock grease or other materials at high temperatures for relatively long periods of time. Its obvious possible disadvantage—that the rate of dissociation might not be sufficient for substantial attainment of equilibrium in the moment required for gas to pass through the heated portion of the nozzle—has been allowed for in the operating procedure, and, moreover, has been shown to be of no consequence in the case of formic acid. (The rate of dissociation of formic acid dimer would be very rapid indeed, if, as seems likely, the energy of activation for the reaction of breaking the hydrogen bonds in the dimer is equal merely to the bond energy of these bonds.)

The nozzle (Fig. 1) was made of 7-mm. Pyrex tubing, and was packed with 1/16″ nichrome helices for a distance of 70 mm. from the capillary end. The packing was held in place by a wad of nichrome wire. The point of entrance of the glass tubing into the camera was sealed with a rubber gasket held in place by a compression nut. Creeping of the glass nozzle up into the camera had to be prevented by a metal band clamped around the glass tubing and bearing against the compression nut. The cold junction, where the thermocouple elements were joined to copper wires, was allowed to stand free in the evacuated camera chamber at a distance of about 10 cm. from the nozzle and was presumed to be at room temperature. The uncertainty of the cold junction temperature was unimportant, since it was only necessary to know the nozzle temperature within 5 or 10 degrees.

The formic acid used was obtained by crystallizing the 98–100% product of the Eastman Kodak Company. The acid was converted to a crystalline slush by chilling, and the crystals were dried by centrifuging. This operation was carried out in a cold room maintained at 6°. By repeating

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[1a] J. M. O'Gorman, W. Shand, Jr., and V. Schomaker, to be published.

[2] J. Karle and L. O. Brockway, THIS JOURNAL, **66**, 574 (1944).