Heats of Combustion of Complex Saturated Hydrocarbons

L. I. BELENYESSY, B. J. GUDZINOWICZ, R. C. REID[1], and J. O. SMITH
Monsanto Research Corp., Everett, Mass.

THE ADVENT OF supersonic aircraft has created a demand for stable, high temperature hydrocarbon fuels with high heats of combustion (*1*). In a current Monsanto research project the physical and thermodynamic properties of many complex, saturated hydrocarbons have been studied (*2*). This article summarizes briefly experimentally determined heats of combustion for many new compounds not heretofore reported and demonstrates the applicability of the Handrick method for correlating such heats of combustion.

EXPERIMENTAL

The five general families of hydrocarbons studied to date are: cyclohexanes, bicyclohexyls, tercyclohexyls, Decalins, and hydrindans. Forty-two compounds belonging to these classes were synthesized at the Monsanto laboratories or purchased from other chemical companies. Heats of combustion were determined with a Parr oxygen bomb calorimeter according to ASTM D 240-57T. Results tabulated in Table I are believed accurate to less than 25 B.t.u. per pound. The values reported for liquids at 77° F. and are net values—the water product is taken to be in vapor form.

HANDRICK METHOD OF DETERMINING HEATS OF COMBUSTION

In 1956, Handrick published a new method for calculating heats of combustion for organic compounds (*3*). The basic premise assumed was that the molar heat of combustion of any organic homologous series bore a straight-line relation to the number of atoms of oxygen lacking in the molecule required to burn the compounds to carbon dioxide and water. Compounds containing sulfur, nitrogen, and the halogens were also covered, but are not considered here. This oxygen requirement for saturated hydrocarbons of the general form C_mH_n is quickly determined:

$$x = 2m + n/2 \qquad (1)$$

The heat of combustion is then computed from the oxygen balance by the following simple equation:

$$Q_c = \sum_i a_i + x\sum_i b_i \qquad (2)$$

Q_c = heat of combustion, kcal. per gram-mole (gross, water product considered a liquid)
x = oxygen requirement from Equation 1
a_i = intercept coefficient for a fuctional group of the ith type
b_i = slope coefficient for a functional group of the ith type

Coefficients a_i and b_i are listed for some 90 functional groups and include differentiation in many cases among liquid, gas, or solid states (*3*). In this same article a complete set of rules is given to allow the best choice of values of a and b for complex structures; for determining Q_c for saturated hydrocarbons, they may be condensed simply:

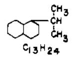
1. For all saturated hydrocarbons, the base values of the a and b terms in Equation 2 are 5.7 and 52.08, respectively.

2. If any chain is branched or if more than one alkyl substituent is attached to a cyclic structure, the values for branched paraffins are added to the a and b values (Table II), but never more than one of these features is to be considered in any molecule.

3. If more than one functional group of the same type is present, the intercept coefficient, a, is multiplied by the number of such groups, but the slope coefficient, b, is the same as for a single group. In cases of conflict between rule 2 and 3, rule 2 is to take precedence.

Table II lists the saturated hydrocarbon functional groups listed by Handrick. In this table are included a and b values for four functional groups—bicyclohexyl, tercyclohexyl, Decalin, and hydrindan. These latter constants were determined by drawing the best straight line through the experimental Q_c values, including all the compounds in each group.

Example of Use of Handrick Method. Consider the estimation of the net heat of combustion of liquid α-isopropyl Decalin at 77° F.

Structure	
Formula	$C_{13}H_{24}$
Molecular weight	180.3

From Equation 1,

$$x = (2)(13) + (24/2) = 38$$
= atoms of oxygen required to burn one molecule of hydrocarbon completely

Functional Groups	a	b
Base value for hydrocarbons	5.7	52.08
Chain branching	−3.7	0.09
Decalin	−13.9	0.00
	$\sum a = -11.9$	$\sum b = 52.17$

From Equation 2,

$$\begin{aligned} Q_c &= (-11.9) + (52.17)\ (38) \\ &= -11.9 + 1982 = 1970 \text{ kcal./gram-mole} \\ &= 3{,}546{,}000 \text{ B.t.u./pound-mole} \end{aligned}$$

To obtain the net heat of combustion, the enthalpy of vaporization of 12 moles of water must be subtracted—i.e., at 77° F., ΔH_v = 18,920 B.t.u./pound-mole.

Thus,

$$\begin{aligned} Q_c \text{ (net)} &= 3{,}546{,}000 - (12)\ (18{,}920) \\ &= 3{,}320{,}000 \text{ B.t.u./pound-mole} \\ &= 18{,}410 \text{ B.t.u./pound} \end{aligned}$$

The observed value is 18,420 B.t.u./pound; the difference is 10 B.t.u./pound.

Table II lists the calculated values of Q_c (net) for all compounds tested. The difference between experimental values and those calculated by the Handrick method is less than 70 B.t.u. per pound (except in three cases) out of about 18,000—i.e., 1 part in ≈250. This method should be applicable to other hydrocarbon series; however, if slope and intercept coefficients for any new functional group in the series are not available, they may be determined from experimental values of Q_c for two members. The calculational method is discussed by Handrick.

---

[1] Present address, Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge 39, Mass.

Table I. Observed and Calculated Heats of Combustion

	$-\Delta H$, B.t.u./Lb. (Net Value at 77° F.)						Estimated Purity of Desired Compound, Mole %^{a}
Compound	Obsd.	Calcd.	Dev. calcd. − obsd.	% cis	% trans	Major Component, Mole %^{a}	
Cyclohexanes							
Diethyl (mixed isomers)	18,650	18,670	+20			95	
1,4-Diethyl (80% cis)	18,670	18,670	0			99.97^{b}	
1,4-Diethyl (70% trans)	18,670	18,670	0			99.95^{b}	
tert-Butyl	18,630	18,680	+50			99.5	
1,2,3,4,5,6-Hexaethyl	18,740	18,700	−40			47.7	99+^{c}
Bicyclohexyls							
Bicyclohexyl	18,440	18,410	−30			99.2	
2-Methyl^{d}	18,420	18,430	+10			98.8	
2-Ethyl^{e}	18,470	18,450	−20			99.9	
4-Ethyl	18,460	18,450	−10			100	
2-*n*-Propyl^{d}	18,470	18,470	0			100	
Isopropyl	18,430	18,470	+40			99	
2,4,6,2′,4′,6′-Hexamethyl	18,540	18,480	−60			44.1	98^{c,f}
4-*n*-Heptyl	18,530	18,520	−10			100	
4-*n*-Nonyl	18,530	18,530	0			99.3	
1,1′-Dimethyl	18,450	18,460	+10			100	
Tercyclohexyls							
o-	18,290	18,290	0			95.6	
m-	18,240	18,290	+50			97.7	
p-	18,320	18,290	−30			91.7	
4′-*n*-Heptyl-*m*-	18,420	18,420	0			99.0	
4′-*n*-Nonyl-*m*-	18,500	18,440	−50			96.8	
Decalins							
cis-	18,300	18,330	+30	99.4	0.5		99.4^{c}
trans-	18,340	18,330	−10	0.1	99.8		99.8^{c}
Mixed isomers	18,360	18,330	−30	57	43		99+^{c}
α-Methyl	18,340	18,300	−40	27.2	71.3		98.5^{c,f}
β-Methyl	18,280	18,300	+20	61.6	37.9		99.5^{c,f}
α-Ethyl	18,370	18,390	+20	31.4	67.8		99.2^{c,f}
β-Ethyl	18,380	18,390	+10	31.7	68.1		99.8^{c,f}
Ethyl	18,370	18,390	+20			40.2	98.7^{c,f}
α-*n*-Propyl	18,380	18,410	+30	32.0	66.2		98.2^{c,f}
α-Isopropyl	18,420	18,410	−10	22.3	76.6		98.9^{c,f}
Isopropyl	18,470	18,410	−60			52.2	99.9+^{c}
α-*n*-Butyl	18,440	18,440	0	25.2	74.3		99.5^{c,f}
α-Isobutyl	18,400	18,440	+40	44.6	54.1		98.7^{c,f}
α-*sec*-Butyl	18,440	18,440	0	37.4	60.9		98.3^{c,f}
tert-Butyl	18,470	18,440	−30			78.1	99.4^{c,f}
Dimethyl	18,430	18,380	+50			37.3	99.9^{c,g}
Hydrindans							
Hydrindan	18,340	18,280	−60			87.2	99.8^{c}
Ethyl	18,430	18,370	−60			50.9	99.4^{c}
Isopropyl	18,320	18,400	+80			56.0	93.5^{c,f}
Diisopropyl	18,490	18,490	0			43.1	98.1^{c,f}
1-Cyclohexyl-3-methyl	18,330	18,280	−50			71.8	99.3^{c,f}
1-Cyclohexyl-1,3,3-trimethyl	18,370	18,340	−30			97.3	97.3^{f}
Miscellaneous structures							
Cyclohexyl (2-ethylcyclohexyl)methane	18,510	18,450	−60			99.8	
1,1-Dicyclohexylheptane	18,550	18,500	−50			95.7	
1,1-Bis(dimethylcyclohexyl)ethane	18,540	18,500	−40			57.3	99+^{c,f}
Cyclohexyl (isopropylcyclohexyl)methane	18,500	18,470	−30			66.7	99.6^{c,f}
Cyclohexyl (ethylcyclohexyl)methane	18,490	18,450	−40			49.2	100^{c}
1-Cyclohexyl-1-isopropylcyclohexylethane	18,470	18,410	−60			65.1	99.5^{c,f}
1,3-Dicyclohexylbutane	18,450	18,470	+20			96	
1,1-Dicyclohexylethane	18,450	18,430	−20			99+	
1,2-Dicyclohexylethane	18,400	18,430	+30			99.7	
1,1-Bis(ethylcyclohexyl)ethane	18,430	18,500	+70			78.8	97.9^{c,f}
Dicyclohexylmethane	18,480	18,410	−70			100	
1,1,3-Tricyclohexylpropane	18,340	18,340	0			99.1	
Bis(ethylcyclohexyl)methane	18,510	18,480	−30			58.8	99.9^{c}
Bis(cyclohexylmethyl)cyclohexane	18,370	18,340	−30			52.9	99.5^{c,f}
2,2-Bis(methylcyclohexyl)propane	18,480	18,480	0			69	99^{c}
1,1-Dicyclohexyl-2-methylpropane	18,540	18,630	+90				99+^{c}
Bis(2,4,6-trimethylcyclohexyl)methane	18,580	18,510	−70				99+^{c}
1-Cyclopentyl-3-cyclohexylpropane	18,410	18,480	+70			99.3	

(Continued)

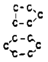
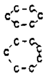
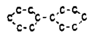
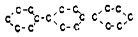
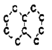
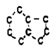
Table I. *(Continued)*

Compound	$-\Delta H$, B.t.u./Lb. (Net Value at 77° F.) Obsd.	Calcd.	Dev. calcd.–obsd.	% cis	% trans	Major Component, Mole %[a]	Estimated Purity of Desired Compound, Mole %[a]
Miscellaneous structures							
1,7,13,19-Eicosatetrayne[h]	18,690	18,720	+30				
1,3,5-Tricyclopentylcyclohexane	18,280	18,330	+50			99+	
1,1-Bis(4-methylcyclohexyl)ethane	18,530	18,470	−60				

[a] All purity checks made with aid of vapor phase chromatography. [b] Both cis- and trans-isomers eluted under one peak; this figure represents mole per cent of both isomers. [c] Vapor phase chromatography showed more than one major peak. Peaks are believed to be isomers of desired compound, and over-all purity of desired material has been estimated. [d] Low boiling isomer. [e] High boiling isomer. [f] Estimated purity of desired compound is minimum figure; actual purity may be higher. [g] Small quantity of ethyl Decalins may be present. [h] Material not investigated by vapor phase chromatography because it exhibited a tendency to explode on heating. [i] Vapor phase chromatography showed four unresolved peaks, probably isomers of desired compound. No purity calculation made.

Table II. Coefficients for Equation 2

Base value for liquid hydrocarbons, $a = 5.7$, $b = 52.08$

Functional group	a	b	Structure[a] (see rule 2)
Branched paraffin[b]	−3.7	+0.09	
Cyclopropane[b]	+16.2	−0.13	
Cyclobutane[b]	+10	+0.11	
Cyclopentane[b]	−1.7	0.00	
Cyclohexane[b]	−7.4	0.00	
Cycloheptane[b]	+17	−0.99	
Bicyclohexyl	−12.0	−0.01	
Tercyclohexyl	−27.6	+0.11	
Decalin	−13.9	0.0	
Hydrindan	−21.2	+0.25	

[a] All carbon atoms may have either hydrocarbon chain or hydrogen attached. [b] Values determined by Handrick (3).

ACKNOWLEDGMENT

The support of this project under U.S. Air Force Contract AF 33(616)-5799 is gratefully acknowledged. The project engineers have been Captain R.D. Haire, Lieutenant T. Gossage, and J. Fultz of the Applications Laboratory, Materials Central, Wright Air Development Divisions.

LITERATURE CITED

(1) Donath, E.E., Hess, M., *Chem. Eng. Progr.* **56**, 68 (1960).
(2) Gollis, M.H., Belenyessy, L.I., Gudzinowicz, B.J., Koch, S.D., Smith, J.O., Wineman, R.J., Abstracts, p. 14R, 138th Meeting, ACS, New York, September 1960.
(3) Handrick, G.R., *Ind. Eng. Chem.* **48**, 1366 (1956).

RECEIVED for review March 8, 1961. Accepted July 26, 1961.

Thermodynamic Properties of Perfluorocyclobutane

JOSEPH J. MARTIN
The University of Michigan, Ann Arbor, Mich.

PERFLUOROCYCLOBUTANE, C_4F_8, is the completely fluorinated derivative of cyclobutane, alternatively known as octafluorocyclobutane and Freon-C318. The compound may be prepared either by cyclic dimerization of tetrafluoroethylene or by pyrolysis of polytetrafluoroethylene. For many potential applications of this compound in refrigeration, heat transfer, and propellents, it is desirable to know the thermodynamic properties. So far one table of such properties has been published (*1*). This is in the German literature, where the units are not those commonly employed in this country, and is based on data that are in some disagreement with the results of this study. Other properties have been investigated and are compared with this work where appropriate. In the work reported here data and equations are developed for the basic properties from which tables and graphs of the thermodynamic properties can easily be calculated.

EXPERIMENTAL WORK AND RESULTS

Experimental measurements were made to determine the vapor pressure, *PVT* behavior of the gas, saturated liquid density, and critical properties. The techniques used were those previously described (*6*). The perfluorocyclobutane was a fractionated material which contained no impurities detectable by infrared analysis. The moisture content was about 0.0005% by weight and the air content of the vapor phase was 0.11% by volume. The heat capacity of the gas was calculated from published spectroscopic data and compared with some experimental data, but no experiments on heat capacity were made in this study.

Vapor Pressure. Data were taken on vapor pressure over the temperature range from 419.94° to 698.85° R. The results have been correlated with an equation which has been shown (*11*) to fit the vapor pressure characteristics of pure compounds with an exceptionally high degree of