

The enthalpies of combustion and formation of some alkyl cyclopropanes^{†‡}

W. D. GOOD

*Bartlesville Petroleum Research Center, Bureau of Mines,
U.S. Department of the Interior, Bartlesville, Oklahoma 74003, U.S.A.*

(Received 4 March 1971)

The enthalpies of combustion of six alkyl cyclopropanes were measured by oxygen-bomb combustion calorimetry. The following values are reported for the standard enthalpy of combustion $\Delta H_c^\circ(298.15\text{ K})/\text{kcal mol}^{-1}$ of these compounds in the liquid state: methylcyclopropane, $-(649.87 \pm 0.14)$; ethylcyclopropane, $-(805.91 \pm 0.18)$; 1,*cis*-2-dimethylcyclopropane, $-(805.55 \pm 0.14)$; 1,*trans*-2-dimethylcyclopropane, $-(804.49 \pm 0.18)$; 1,1,2-trimethylcyclopropane, $-(951.21 \pm 0.18)$; 1,1,2,2-tetramethylcyclopropane, $-(1107.94 \pm 0.20)$. Values of the enthalpy of formation of the liquids were derived.

1. Introduction

The Bureau of Mines is studying the thermodynamic properties of small organic molecules with high ring-strain energy. In the present study the effect of methyl and ethyl substitution on cyclopropane has been investigated. Enthalpies of formation of the substituted cyclopropanes were compared with those of similarly substituted cyclopentanes and cyclohexanes.

2. Experimental

APPARATUS AND PROCEDURES

Experimental measurements of the enthalpy of combustion followed procedures recently reported.⁽¹⁻³⁾ The rotating-bomb calorimeter BMR II⁽⁴⁾ and platinum-lined bomb Pt-3b,⁽⁵⁾ internal volume 0.349_4 dm^3 , have been described. The bomb was not rotated. Water (1 cm^3) was added to the bomb, and the bomb was flushed and charged to 30 atm with pure oxygen. § Formation of nitric acid was minimized by use of pure oxygen. Each experiment was started at 23°C , and because of the masses of combustibles chosen, the final temperatures were nearly 25°C .

Fragile borosilicate glass ampoules with flexible walls⁽⁶⁾ were used for experiments on ethylcyclopropane, 1,*cis*-2-dimethylcyclopropane, 1,*trans*-2-dimethylcyclopropane, 1,1,2-trimethylcyclopropane, and 1,1,2,2-tetramethylcyclopropane.

[†] Work conducted in part under an Interservice Support Agreement between the Air Force Office of Scientific Research, Office of Aerospace Research, U.S. Air Force, Contract No. AFOSR-ISSA-70-0001, Project 9750, Task No. 02, and the Bureau of Mines, U.S. Department of the Interior.

[‡] Contribution No. 184 from the thermodynamics laboratory of the Bartlesville Petroleum Research Center.

§ atm = $101\,325\text{ N m}^{-2}$.

The normal boiling temperatures of ethylcyclopropane, 1,*cis*-2-dimethylcyclopropane, and 1,*trans*-2-dimethylcyclopropane are 35.93, 37.03, and 28.21 °C, respectively,⁽⁷⁾ and materials of this volatility are difficult to seal cleanly in flexible glass ampoules at room temperature; therefore, ampoules with abnormally large, flattened sides were prepared and sealed full of liquid at 15 °C. The ampoule sides flexed as the samples warmed to room temperature. Clean seals were obtained by this procedure. Samples of 1,1,2-trimethylcyclopropane and 1,1,2,2-tetramethylcyclopropane, boiling at 52.44 and 71 °C, respectively, were sealed in flexible ampoules at room temperature (25 °C).

Methylcyclopropane, boiling at 0.73 °C, required rigid ampoules that were filled by a new method. Each ampoule, of known internal volume, was sealed to a small ground-glass joint. The joint and ampoule were subsequently weighed, and the ampoules were attached to a high vacuum system. Methylcyclopropane was condensed into each of the ampoules which were in turn sealed at -77 °C and allowed to warm to room temperature. A small vapor space was left inside each ampoule. The sealed ampoule and its ground-glass joint were again weighed, and since the internal volume was known, the apparent weight could be reduced to mass.

Carbon dioxide was recovered from each of the combustion experiments (table 1), but sample mass was used as the measure of the amount of reaction. The amount of

TABLE 1. Carbon dioxide recovery

Compound	Per cent recovery
Benzoic acid (25) ^a	100.00 ₂ ± 0.01 ₂ ^b
Methylcyclopropane (7)	99.97 ₂ ± 0.02 ₃
Ethylcyclopropane (6)	99.96 ₄ ± 0.01 ₇
1, <i>cis</i> -2-Dimethylcyclopropane (7)	99.96 ₈ ± 0.02 ₂
1, <i>trans</i> -2-Dimethylcyclopropane (7)	99.98 ₈ ± 0.01 ₃
1,1,2-Trimethylcyclopropane (6)	100.00 ₁ ± 0.00 ₉
1,1,2,2-Tetramethylcyclopropane (6)	99.99 ₉ ± 0.00 ₅

^a Number of experiments.

^b Average deviation from the mean.

carbon dioxide recovered served as a measure of the purity of the sample and the completeness of the combustion reaction. The combustion products were analyzed for carbon monoxide or other products of incomplete combustion, but none were detected. The carbon dioxide recoveries for the four more volatile compounds were slightly lower than normal, and the spread of the determinations was greater, but there was no apparent correlation between carbon dioxide recovery and the enthalpy of combustion for the individual experiments.

MATERIALS

The compounds were samples of API research hydrocarbons purified and made available by American Petroleum Institute Research Project 58 at Carnegie-Mellon University, A. J. Streiff, Director. Sample designations and impurities given by API Project 58 are listed in table 2.

TABLE 2. Compound description

Compound	Moles per cent of impurity
Methylcyclopropane	0.018 ± 0.004
Ethylcyclopropane	0.25 ± 0.02
1, <i>cis</i> -2-Dimethylcyclopropane	0.09 ± 0.05
1, <i>trans</i> -2-Dimethylcyclopropane	0.23 ± 0.12
1,1,2-Trimethylcyclopropane	0.12 ± 0.08
1,1,2,2-Tetramethylcyclopropane	0.04 ± 0.03

Each compound was dried by means of a vapor pass over P_2O_5 before ampoules were filled.

The auxiliary oil, sample designation USBM-P3a, had the empirical formula $CH_{1.894}$. For this material $\Delta E_c^\circ/M = -(10984.3_0 \pm 0.1_5)$ cal g^{-1} (mean and standard deviation). For the cotton thread fuse, empirical formula $CH_{1.774}O_{0.887}$, $\Delta E_c^\circ/M$ was -4050 cal g^{-1} .

CALIBRATION

The calorimeter was calibrated with benzoic acid, NBS Sample 39i, which has an energy of combustion of $-(26.434 \pm 0.003)$ kJ g^{-1} under certificate conditions. Conversion to standard conditions⁽⁸⁾ gives $-(6313.02 \pm 0.72)$ cal g^{-1} for $\Delta E_c^\circ/M$, the energy of the idealized combustion reaction. The cyclopropanes were studied in four series of experiments, and a calibration series was completed with each series of cyclopropanes. The series and the corresponding values of $\epsilon(\text{calor})$ are tabulated in table 3. No known changes occurred in the calorimeter between series.

TABLE 3. Energy equivalent of calorimeter

Compound	$\epsilon(\text{calor})/\text{cal K}^{-1}$
Methylcyclopropane (6) ^a	4005.30 ± 0.20 ^b
Ethylcyclopropane (6)	4005.38 ± 0.25
1, <i>cis</i> -2-Dimethylcyclopropane (7)	4005.36 ± 0.18
1, <i>trans</i> -2-Dimethylcyclopropane	
1,1,2-Trimethylcyclopropane (7)	4005.17 ± 0.18
1,1,2,2-Tetramethylcyclopropane	

^a Number of calibration experiments.

^b Mean value with standard deviation.

UNITS OF MEASUREMENT AND AUXILIARY QUANTITIES

The experimental results are based on 1961 atomic weights⁽⁹⁾ and the definitions $0^\circ\text{C} \cong 273.15\text{ K}$ and $1\text{ cal} = 4.184\text{ J}$.⁽¹⁰⁾

TABLE 4. Physical properties at 298.15 K

Compound	ρ g cm ⁻³	$(\partial E/\partial P)_T$ cal atm ⁻¹ g ⁻¹	c_P cal K ⁻¹ g ⁻¹
Methylcyclopropane	0.634 ^a	(—) ^b	0.55
Ethylcyclopropane	0.679 ^c	-0.0072	0.54
1, <i>cis</i> -2-Dimethylcyclopropane	0.6889 ^c	-0.0072	0.54
1, <i>trans</i> -2-Dimethylcyclopropane	0.6648 ^c	-0.0072	0.54
1,1,2-Trimethylcyclopropane	0.6897 ^c	-0.0072	0.53
1,1,2,2-Tetramethylcyclopropane	0.702 ^b	-0.0072	0.52

^a Measurements of this laboratory.

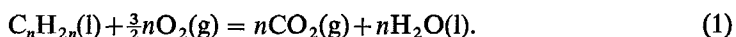
^b All experiments were performed with rigid ampoules.

^c Reference 7.

For reducing weights in air to masses, converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states,⁽⁸⁾ the values in table 4 were used for density ρ , specific heat capacity c_P , and $(\partial E/\partial P)_T$. Values of $(\partial E/\partial P)_T$ were calculated from the temperature dependence of density by use of the approximation, $(\partial E/\partial P)_T = -T(\partial V/\partial T)_P$. The values of heat capacity are estimates.

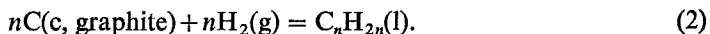
3. Calorimetric results

Typical experimental results for each of the cyclopropanes are summarized in table 5. It is impractical to list summaries for all experiments, but values of $\Delta E_c^\circ/M$ for all experiments are tabulated in table 6. Standard deviations of the mean are given. All values of $\Delta E_c^\circ/M$ refer to the unit mass of sample. Values of $\Delta E_c^\circ/M$ (tables 5 and 6) refer to equation (1):



4. Derived results

The derived molar values for the cyclopropanes are given in table 7. Values of $\Delta E_c^\circ(298.15 \text{ K})$, the energy of the idealized combustion reaction, and $\Delta H_c^\circ(298.15 \text{ K})$, the standard enthalpy of combustion, refer to equation (1). The values of the enthalpies of formation refer to equation (2):



Uncertainties expressed are the "uncertainty interval".⁽¹¹⁾ The enthalpies of formation of gaseous CO_2 and liquid H_2O were taken to be -94.051 and $-68.315 \text{ kcal mol}^{-1}$, respectively.⁽¹²⁾ Uncertainties assigned to gaseous carbon dioxide⁽¹³⁾ and liquid water⁽¹⁴⁾ were 0.011 and $0.010 \text{ kcal mol}^{-1}$, respectively.

TABLE 5. Summary of typical calorimetric experiments at 298.15 K ^a

	Methyl- cyclopropane	Ethyl- cyclopropane	1, <i>cis</i> -2- Dimethyl- cyclopropane	1, <i>trans</i> -2- Dimethyl- cyclopropane	1,1,2- Trimethyl- cyclopropane	1,1,2,2- Tetramethyl- cyclopropane
$m'(\text{compound})/\text{g}$	0.548 029	0.616 218	0.633 519	0.640 122	0.656 938	0.632 822
$m''(\text{oil})/\text{g}$	0.153 278	0.086 674	0.067 828	0.063 280	0.056 208	0.081 811
$m''(\text{fuse})/\text{g}$	0.001 218	0.000 986	0.001 428	0.001 152	0.001 278	0.001 283
$n(\text{H}_2\text{O})/\text{mol}$	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
$\Delta t_c/\text{K} = (t_f - t_i + \Delta t_{\text{corr}})/\text{K}$	2.00144	2.00139	1.99895	2.00267	2.00389	2.00338
$q(\text{calor})/(-\Delta t_c)/\text{cal}$	-8016.36	-8016.31	-8006.51	-8021.39	-8025.93	-8023.87
$q(\text{cont})/(-\Delta t_c)/\text{cal}^b$	-10.46	-10.41	-10.39	-10.41	-9.99	-9.98
$\Delta E_{\text{ign}}/\text{cal}$	0.53	0.49	0.79	0.71	0.47	0.59
$\Delta E_{\text{deo}}(\text{HNO}_3)/\text{cal}$	0.00	0.00	0.00	0.00	0.00	0.00
$\Delta E_{\text{corr to acid states}}/\text{cal}^c$	2.23	2.26	2.25	2.25	2.30	2.31
$-m''(\Delta E_c^0/M)(\text{oil})/\text{cal}$	1683.65	952.05	745.05	695.08	617.41	898.64
$-m''(\Delta E_c^0/M)(\text{fuse})/\text{cal}$	4.93	3.99	5.78	4.66	5.18	5.20
$m'(\Delta E_c^0/M)(\text{compound})/\text{cal}$	-6335.48	-7067.93	-7263.03	-7329.10	-7410.56	-7127.11
$m'(\Delta E_c^0/M)(\text{compound})/\text{cal g}^{-1}$	-11560.49	-11469.86	-11464.58	-11449.53	-11280.45	-11262.43

^a The symbols and abbreviations of this table are those of reference 8 except as noted.^b $q(\text{cont})/(t_f - 25^\circ\text{C}) + q(\text{cont}) (25^\circ\text{C} - t_f + \Delta t_{\text{corr}})$.^c Items 81 to 85, 87 to 90, 93, and 94 of the computation form of reference 8.

TABLE 6. Summary of experimental results. Values of $(\Delta E^\circ_f/M)/\text{cal g}^{-1}$ at 298.15 K

	Methyl- cyclopropane	Ethyl- cyclopropane	1, <i>cis</i> -2- Dimethyl- cyclopropane	1, <i>trans</i> -2- Dimethyl- cyclopropane	1,1,2- Trimethyl- cyclopropane	1,1,2,2- Tetramethyl- cyclopropane
	-11564.01	-11467.12	-11464.58	-11448.97	-11279.00	-11261.34
	-11559.57	-11469.83	-11467.18	-11444.79	-11281.96	-11260.90
	-11560.49	-11469.16	-11463.20	-11452.20	-11279.70	-11265.30
	-11559.62	-11469.36	-11465.40	-11451.37	-11281.14	-11262.47
	-11562.50	-11469.86	-11463.77	-11450.56	-11280.45	-11262.75
	-11564.59	-11472.87	-11463.79	-11448.68	-11283.53	-11262.43
	-11558.55		-11463.36	-11449.53		
Mean:	-11561.33	-11469.70	-11464.45	-11449.44	-11280.96	-11262.53
Standard deviation:	0.89	0.76	0.53	0.91	0.67	0.63

TABLE 7. Derived molar values at 298.15 K

Compound	$\frac{\Delta E^\circ_f(l)}{\text{kcal mol}^{-1}}$	$\frac{\Delta H^\circ_f(l)}{\text{kcal mol}^{-1}}$	$\frac{\Delta H^\circ_f(l)}{\text{kcal mol}^{-1}}$
Methylcyclopropane	-648.69 ± 0.14	-649.87 ± 0.14	$+0.41 \pm 0.16$
Ethylcyclopropane	-804.43 ± 0.18	-805.91 ± 0.18	-5.92 ± 0.19
1, <i>cis</i> -2-Dimethylcyclopropane	-804.06 ± 0.14	-805.55 ± 0.14	-6.29 ± 0.16
1, <i>trans</i> -2-Dimethylcyclopropane	-803.01 ± 0.18	-804.49 ± 0.18	-7.34 ± 0.19
1,1,2-Trimethylcyclopropane	-949.43 ± 0.18	-951.21 ± 0.18	-22.99 ± 0.20
1,1,2,2-Tetramethylcyclopropane	-1105.86 ± 0.20	-1107.94 ± 0.20	-28.63 ± 0.22

5. Discussion

The enthalpies of formation of several liquid cyclopropanes, cyclopentanes, and cyclohexanes and their differences are tabulated in table 8. Enthalpies of vaporization are not yet available for the cyclopropanes; therefore, comparisons cannot be made in the ideal gaseous state. Enthalpies of combustion of cyclopentane and cyclohexane with 1,1,2-trimethyl and 1,1,2,2-tetramethyl substitution have not been reported.

A recent study of Tomareva *et al.*⁽¹⁶⁾ found $0.8 \text{ kcal mol}^{-1}$ difference in the enthalpies of formation of the *cis*- and *trans*-isomers of 1,2-dimethyl-3,3-dichlorocyclopropane. The present study found $1.06 \text{ kcal mol}^{-1}$ difference in the enthalpies of formation of *cis*- and *trans*-1,2-dimethylcyclopropane. Agreement of the two values is well within the combined uncertainties.

REFERENCES

1. Good, W. D. *J. Chem. Thermodynamics* **1970**, 2, 237.
2. Good, W. D. *J. Chem. Eng. Data* **1969**, 14, 231.
3. Good, W. D.; Smith, N. K. *J. Chem. Eng. Data* **1969**, 14, 102.
4. Good, W. D.; Scott, D. W.; Waddington, G. *J. Phys. Chem.* **1956**, 60, 1080.
5. Good, W. D.; Douslin, D. R.; Scott, D. W.; George, A.; Lacina, J. L.; Dawson, J. P.; Waddington, G. *J. Phys. Chem.* **1959**, 63, 1133.
6. Guthrie, G. B.; Scott, D. W.; Hubbard, W. N.; Katz, C.; McCullough, J. P.; Gross, M. E.; Williamson, K. D.; Waddington, G. *J. Amer. Chem. Soc.* **1952**, 74, 4662.
7. *Selected Values of Properties of Hydrocarbons and Related Compounds*, American Petroleum Institute Research Project 44, Chemical Thermodynamics Properties Center, Texas A & M University, College Station, Texas (loose-leaf sheets, extant, **1970**).
8. Hubbard, W. N.; Scott, D. W.; Waddington, G. In *Experimental Thermochemistry*, Chap. 5. F. D. Rossini; editor. Interscience: New York. **1956**, pp. 75-128.
9. Cameron, A. E.; Wichers, E. *J. Amer. Chem. Soc.* **1962**, 84, 4175.
10. Cohen, E. R.; DuMond, J. W. M. *Rev. Mod. Phys.* **1965**, 37, 537.
11. Rossini, F. D. In *Experimental Thermochemistry*, Chap. 14. F. D. Rossini; editor. Interscience: New York. **1956**, pp. 297-320.
12. Wagman, D. D.; Evans, W. H.; Halow, I.; Parker, V. B.; Bailey, S. M.; Schumm, R. H. *Nat. Bur. Stand. (U.S.) Tech. Note* 270-3, **1968**.
13. Rossini, F. D.; Jessup, R. S. *J. Res. Nat. Bur. Stand.* **1938**, 21, 491.
14. Rossini, F. D. *J. Res. Nat. Bur. Stand.* **1931**, 6, 1.
15. Ruehrwein, R. A.; Powell, T. M. *J. Amer. Chem. Soc.* **1946**, 68, 1063.
16. Tomareva, E. M.; Kolesov, V. P.; Nefedov, O. M.; Skuratov, S. M. *Zh. Fiz. Khim.* **1968**, 42, 2611.