J. Chem. Thermodynamics **1974**, 6, 303–310

The enthalpies of formation of ethylcyclobutane, methylenecyclobutane, and 1,1-dimethylcyclopropane[a,b]

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(*Received 20 June 1973*)

The enthalpies of combustion of ethylcyclobutane, methylenecyclobutane, and 1,1-dimethylcyclopropane were measured by oxygen-bomb combustion calorimetry. The following values are reported for the standard enthalpy of combustion $\Delta H_c^\circ(298.15\ \mathrm{K})/\mathrm{kcal_{th}\ mol^{-1}}$,† of these compounds in the liquid state: ethylcyclobutane, $-(960.11 \pm 0.16)$; methylenecyclobutane, $-(765.95 \pm 0.12)$; 1,1-dimethylcyclopropane, $-(803.86 \pm 0.17)$. The enthalpy of vaporization of methylenecyclobutane was derived from vapor pressure measurements, and enthalpies of vaporization of ethylcyclobutane and 1,1-dimethylcyclopropane were estimated. Values of the enthalpy of formation in the liquid and gaseous states were derived for all three compounds. Ring-strain energy was estimated. Some regularities and irregularities in the accepted values of enthalpies of combustion of the alkylcyclopropanes and alkylcyclobutanes indicate an error in a previous determination of the enthalpy of formation of methylcyclobutane.

1. Introduction

The thermodynamic properties of small organic molecules with high ring-strain energy are being studied as part of a Bureau of Mines program that investigates materials delivering relatively high energies upon combustion. As a result of these studies, the enthalpies of formation of six alkyl cyclopropanes have been reported.(1) In the present study, another alkyl cyclopropane was investigated, and study of the cyclobutanes was commenced. Techniques were used that have been described.(1)

Comparison of the enthalpies of formation of ethylcyclobutane and 1,1-dimethylcyclopropane with existing enthalpies of formation, both from the earlier research of this laboratory and from the compilation of Cox and Pilcher,(2) showed striking regularities and irregularities within the alkyl-substituted cyclopropanes, cyclobutanes, cyclopentanes, and cyclohexanes.

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[a] Work conducted under an Interservice Agreement between the Air Force Office of Scientific Research, Office of Aerospace Research, U.S. Air Force, Contract No. AFOSR-ISSA-71-0001, Project 9750, Task No. 01, and the Bureau of Mines, U.S. Department of the Interior.

[b] Contribution No. 202 from the energy relationships laboratory of the Bartlesville Energy Research Center.

† Throughout this paper $\mathrm{cal_{th}} = 4.184$ J; atm = 101 325 Pa.

Strain energies were calculated for ethylcyclobutane, methylenecyclobutane, and 1,1-dimethylcyclopropane and compared with ring-strain energies in the bare cyclopropane and cyclobutane rings.

2. Experimental

APPARATUS AND PROCEDURES

The rotating-bomb calorimeter BMR II,(3) and platinum-lined bomb Pt-3b,(4) internal volume 0.349_4 dm^3, have been described.

Experimental measurements of the enthalpy of combustion followed procedures already described.(5–7) 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 296.15 K, and because of the masses of combustibles chosen, the final temperatures were nearly 298.15 K.

Fragile borosilicate-glass ampoules with flexible walls(8) were used for ethylcyclobutane and methylenecyclobutane. 1,1-Dimethylcyclopropane, boiling at 294.15 K, required rigid ampoules.(1)

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

TABLE 1. Carbon dioxide recovery: $r = n(\mathrm{CO_2}, \text{recovered})/n(\mathrm{CO_2}, \text{calculated})$

Compound	No. of experiments	$100r$ [a]
Ethylcyclobutane	5	$99.97_0 \pm 0.01_1$
Benzoic acid	6	$100.00_7 \pm 0.00_4$
Methylenecyclobutane	8	$100.00_1 \pm 0.00_6$
Benzoic acid	7	$100.00_3 \pm 0.00_3$
1,1-Dimethylcyclopropane	5	$99.97_0 \pm 0.00_7$
Benzoic acid	5	$100.00_6 \pm 0.00_6$

[a] With standard deviation from the mean.

The combustion products were analyzed for carbon monoxide or other products of incomplete combustion, but none was detected. The essentially quantitative carbon dioxide recoveries serve as a measure of the completeness of the reaction and purity of the sample, except for possible isomeric impurity.

MATERIALS

Ethylcyclobutane was an API research hydrocarbon (API Standard Sample 1153–5S) purified and made available by American Petroleum Institute Research Project 58 at Carnegie-Mellon University, A. J. Streiff, Director. Sample impurity given by API Project 58 was (0.08 ± 0.06) mole per cent.

Methylenecyclobutane was obtained as the by-product of the synthesis of its isomer, spiropentane.(9) Gas-liquid-chromatographic purification of the crude material was followed by distillation. The resulting sample was studied by the Low-Temperature

Calorimetry Group of the Center, and analysis of the plot of the melting temperature against fraction-melted indicated an impurity of 0.35 mole per cent. The probable impurity is isomeric spiropentane.

1,1-Dimethylcyclopropane was obtained commercially. Preparatory gas-liquid chromatography produced material such that subsequent analytical gas-liquid chromatography indicated an impurity of 0.04 mole per cent.

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

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[(10)] gives $-(6313.02 \pm 0.72)$ $cal_{th}\, g^{-1}$ for $\Delta E_c^\circ/M$, the energy of the idealized combustion reaction. Six calibration experiments performed during the ethylcyclobutane experiments gave ε(calor) = (4005.77 ± 0.22) $cal_{th}\, K^{-1}$ (mean and standard deviation). Seven calibration experiments for the methylenecyclobutane series gave ε(calor) = (4006.02 ± 0.09) $cal_{th}\, K^{-1}$. Before the experiments with 1,1-dimethylcyclopropane, the compression ring for the bomb was replaced with a more massive ring, and ε(calor) increased to (4007.05 ± 0.26) $cal_{th}\, K^{-1}$ for the 1,1-dimethylcyclopropane experiments.

UNITS OF MEASUREMENT AND AUXILIARY QUANTITIES

The experimental results are based on 1961 atomic weights[(11)] and the definition $cal_{th} = 4.184$ J.[(12)]

For reducing apparent masses in air to masses, converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states,[(10)] the values in table 2 were used for density ρ, specific heat capacity c_p, and $(\partial E/\partial p)_T$.

TABLE 2. Physical properties at 298.15 K
(cal_{th} = 4.184 J, atm = 101.325 kPa)

Compound	ρ / g cm^{-3}	$(\partial E/\partial p)_T$ / cal_{th} atm^{-1} g^{-1}	c_p / cal_{th} K^{-1} g^{-1}
Ethylcyclobutane	0.7232	0.0129	0.46
Methylenecyclobutane	0.740	0.013	0.46
1,1-Dimethylcyclopropane	0.6554	(—)[a]	0.46

[a] Rigid ampoules were used.

Densities of ethylcyclobutane and 1,1-dimethylcyclopropane are taken from the tables of API Research Project 44.[(13)] The density of methylenecyclobutane was measured in this laboratory. The value of $(\partial E/\partial p)_T$ for ethylcyclobutane was calculated from the temperature dependence of density[(13)] by use of the approximation, $(\partial E/\partial p)_T = -T(\partial V/\partial T)_p$. All other values are estimates.

3. Calorimetric results

Typical experimental results for each of the compounds are given in table 3. It is impractical to list summaries for all experiments, but values of $\Delta E_c^\circ/M$ for all experiments are tabulated in table 4. Standard deviations of the mean are given. The values of $\Delta E_c^\circ/M$ refer to unit mass of sample and to the following equations:

Ethylcyclobutane:

$$C_6H_{12}(l)+9O_2(g) = 6CO_2(g)+6H_2O(l), \tag{1}$$

TABLE 3. Summary of typical calorimetric experiments at 298.15 K [a]
($\mathrm{cal_{th}} = 4.184$ J)

	Ethylcyclobutane	Methylene-cyclobutane	1,1-Dimethyl-cyclopropane
m'(compound)/g	0.634535	0.489359	0.586665
m''(oil)/g	0.071346	0.230323	0.118647
m'''(fuse)/g	0.001062	0.001186	0.001344
$n^i(H_2O)$/mol	0.05535	0.05535	0.05535
$\Delta T_c/\mathrm{K} = (T_f - T_i + \Delta T_{corr})/\mathrm{K}$	1.99853	2.00235	1.99972
ε(calor)$(-\Delta T_c)/\mathrm{cal_{th}}$	−8005.64	−8021.45	−8012.96
ε(cont)$(-\Delta T_c)/\mathrm{cal_{th}}$ [b]	−10.10	−10.19	−10.57
$\Delta E_{ign}/\mathrm{cal_{th}}$	0.47	0.45	0.53
$\Delta E_{dec}(HNO_3)/\mathrm{cal_{th}}$	0.00	0.00	0.00
ΔE(corr to std states)$/\mathrm{cal_{th}}$ [c]	2.17	2.62	2.40
$-m''(\Delta E_c^\circ/M)$(oil)$/\mathrm{cal_{th}}$	783.69	2529.93	1303.25
$-m'''(\Delta E_c^\circ/M)$(fuse)$/\mathrm{cal_{th}}$	4.30	4.80	5.44
$m'(\Delta E_c^\circ/M)$(compound)$/\mathrm{cal_{th}}$	−7225.11	−5493.84	−6711.91
$(\Delta E_c^\circ/M)$(compound)$/\mathrm{cal_{th}\ g^{-1}}$	−11386.47	−11226.61	−11440.78

[a] The symbols and abbreviations of this table are those of reference 10 except as noted.
[b] $\varepsilon^i(\mathrm{cont})(T_i - 298.15\ \mathrm{K}) - \varepsilon^f(\mathrm{cont})(298.15\ \mathrm{K} - T_f - \Delta T_{corr})$.
[c] Items 81 to 85, 87 to 90, 93, and 94 of the computation form of reference 10.

TABLE 4. Summary of experimental results at 298.15 K
($\mathrm{cal_{th}} = 4.184$ J)

	$(\Delta E_c^\circ/M)/\mathrm{cal_{th}\ g^{-1}}$		
	Ethylcyclobutane	Methylenecyclobutane	1,1-Dimethylcyclopropane
	−11386.47	−11226.61	−11440.78
	−11387.13	−11225.14	−11440.73
	−11385.64	−11226.26	−11437.84
	−11387.59	−11228.18	−11440.43
	−11386.67	−11229.17	−11442.51
		−11225.18	
		−11227.59	
		−11225.95	
Mean:	−11386.70	−11226.75	−11440.46
Standard deviation:	0.33	0.51	0.75

methylenecyclobutane:

$$C_5H_8(l)+7O_2(g) = 5CO_2(g)+4H_2O(l), \tag{2}$$

and 1,1-dimethylcyclopropane:

$$C_5H_{10}(l)+(15/2)O_2(g) = 5CO_2(g)+5H_2O(l). \tag{3}$$

4. Enthalpies of vaporization

The ebulliometric method was used to determine the vapor pressure of methylenecyclobutane.(14, 15) The enthalpy of vaporization at 298.15 K, (6.62 ± 0.10) $\mathrm{kcal_{th}\,mol^{-1}}$, was computed from the Cox equation,(16) the exact form of the Clapeyron equation, and an estimate of the second virial coefficient.

The enthalpies of vaporization of ethylcyclobutane and 1,1-dimethylcyclopropane, estimated by use of Wadsö's equation(17) and the incremental method, were (7.8 ± 0.2) and (6.0 ± 0.2) $\mathrm{kcal_{th}\,mol^{-1}}$, respectively.

5. Derived results

The derived molar values for the compounds are given in table 5. No earlier experimental values are available for comparison. Values of $\Delta E_c^\circ(298.15\ \mathrm{K})$, the standard energy of the idealized combustion reaction, and $\Delta H_c^\circ(298.15\ \mathrm{K})$, the standard enthalpy of combustion, refer to equations (1), (2), and (3). The values of the enthalpy of formation refer to the following equations:

TABLE 5. Derived molar values at 298.15 K
($\mathrm{cal_{th}} = 4.184$ J)

	Ethylcyclobutane	Methylenecyclobutane	1,1-Dimethylcyclopropane
$\Delta E_c^\circ(l)/\mathrm{kcal_{th}\,mol^{-1}}$	-958.33 ± 0.16	-764.76 ± 0.12	-802.38 ± 0.17
$\Delta H_c^\circ(l)/\mathrm{kcal_{th}\,mol^{-1}}$	-960.11 ± 0.16	-765.95 ± 0.12	-803.86 ± 0.17
$\Delta H_f^\circ(l)/\mathrm{kcal_{th}\,mol^{-1}}$	-14.09 ± 0.18	22.43 ± 0.14	-7.97 ± 0.19
$\Delta H_v^\circ/\mathrm{kcal_{th}\,mol^{-1}}$	7.8 ± 0.2	6.62 ± 0.10	6.0 ± 0.2
$\Delta H_f^\circ(g)/\mathrm{kcal_{th}\,mol^{-1}}$	$-6.2_9 \pm 0.2_7$	29.05 ± 0.17	$-1.9_7 \pm 0.2_8$

Ethylcyclobutane:

$$6C(c, \text{graphite})+6H_2(g) = C_6H_{12}(l \text{ or } g), \tag{4}$$

methylenecyclobutane:

$$5C(c, \text{graphite})+4H_2(g) = C_5H_8(l \text{ or } g), \tag{5}$$

and 1,1-dimethylcyclopropane:

$$5C(c, \text{graphite})+5H_2(g) = C_5H_{10}(l \text{ or } g). \tag{6}$$

Uncertainties expressed are the "uncertainty interval".(18) The enthalpies of formation of gaseous CO_2 and liquid H_2O were taken to be -94.051 and -68.315 $\mathrm{kcal_{th}\ mol^{-1}}$, respectively.(19) Uncertainties assigned to $CO_2(g)$(20) and $H_2O(l)$(21) were 0.011 and 0.010 $\mathrm{kcal_{th}\ mol^{-1}}$, respectively.

6. Strain energies

Enthalpies of atomization were estimated by the unified four-parameter scheme discussed by Cox and Pilcher.(2) Estimated enthalpies of atomization are compared with experimental enthalpies of atomization in table 6. Differences between the estimated and experimental values are the strain energy that arises from the ring itself and from interactions of the substituents attached to the ring. Ring-strain energies for cyclopropane and cyclobutane are listed for comparison.

TABLE 6. Strain energies E_{strain} in compounds
($\mathrm{cal_{th}} = 4.184$ J)

	ΔH_a(obs) $\mathrm{kcal_{th}\ mol^{-1}}$	ΔH_a(est) $\mathrm{kcal_{th}\ mol^{-1}}$	E_{strain} $\mathrm{kcal_{th}\ mol^{-1}}$
Ethylcyclobutane	1656.89	1682.14	25.3
Methylenecyclobutane	1242.25	1269.90	27.7
1,1-Dimethylcyclopropane	1377.47	1405.62	28.2
Cyclobutane	1093.62	1120.08	26.5
Cyclopropane	812.57	840.06	27.5

7. Regularities and irregularities in the cyclopropanes and cyclobutanes

The enthalpies of combustion of liquid cyclopropane, cyclobutane, cyclopentane, cyclohexane, and their methyl- and ethy-derivatives are given in table 7. The values for the homologous series increase regularly, except for methylcyclobutane. The value for cyclopropane is derived from the flame calorimetry of Rossini and Knowlton(22) coupled with an enthalpy of vaporization derived from the research of Ruehrwein and Powell.(23) Values for methylcyclopropane,(1) ethylcyclopropane,(1) and ethylcyclobutane are from the research of this laboratory. All other values are the "selected values" of Cox and Pilcher,(2) selections made from the literature on experimental evidence only. The value for liquid methylcyclobutane, based on the research of Humphrey and Spitzer,(24) is an apparent misfit.

The enthalpies of combustion of liquid cyclopropane, cyclopentane, cyclohexane, and their dimethyl derivatives are compared in table 8. The value for cyclopropane has been identified. Values for the dimethylcyclopropanes(1) are from the research of this laboratory. All other values are those selected by Cox and Pilcher.(2) The interaction of methyl and ethyl substituents with the rigid cyclopropane ring at one extreme is undoubtedly different from the interaction with the flexible cyclohexane ring at the other extreme, but the parallelism still is evident.

TABLE 7. Enthalpies of combustion of liquid cycloalkanes at 298.15 K
($\mathrm{cal_{th}} = 4.184$ J)

	Cyclopropanes		Cyclobutanes		Cyclopentanes		Cyclohexanes	
	$\frac{-\Delta H^\circ_c(\mathrm{l})}{\mathrm{kcal_{th}\ mol^{-1}}}$	$\frac{-\Delta\{\Delta H^\circ_c(\mathrm{l})\}}{\mathrm{kcal_{th}\ mol^{-1}}}$	$\frac{-\Delta H^\circ_c(\mathrm{l})}{\mathrm{kcal_{th}\ mol^{-1}}}$	$\frac{-\Delta\{\Delta H^\circ_c(\mathrm{l})\}}{\mathrm{kcal_{th}\ mol^{-1}}}$	$\frac{-\Delta H^\circ_c(\mathrm{l})}{\mathrm{kcal_{th}\ mol^{-1}}}$	$\frac{-\Delta\{\Delta H^\circ_c(\mathrm{l})\}}{\mathrm{kcal_{th}\ mol^{-1}}}$	$\frac{-\Delta H^\circ_c(\mathrm{l})}{\mathrm{kcal_{th}\ mol^{-1}}}$	$\frac{-\Delta\{\Delta H^\circ_c(\mathrm{l})\}}{\mathrm{kcal_{th}\ mol^{-1}}}$
Cycloalkane	495.09		650.35		786.54		936.80	
		154.78		150.85		154.81		154.33
Methylcycloalkane	649.87		801.20		941.35		1091.13	
		156.04		158.91		156.15		157.10
Ethylcycloalkane	805.91		960.11		1097.50		1248.23	

TABLE 8. Enthalpies of combustion of liquid cycloalkanes and dimethylcycloalkanes at 298.15 K
($\mathrm{cal_{th}} = 4.184$ J)

	Cyclopropanes		Cyclopentanes		Cyclohexanes	
	$\frac{-\Delta H\ \ \mathrm{l})}{\mathrm{kcal_{th}\ mol^{-1}}}$	$\frac{-\Delta\{\Delta H^\circ_c(\mathrm{l})\}}{\mathrm{kcal_{th}\ mol^{-1}}}$	$\frac{-\Delta H^\circ_c(\mathrm{l})}{\mathrm{kcal_{th}\ mol^{-1}}}$	$\frac{-\Delta\{\Delta H^\circ_c(\mathrm{l})\}}{\mathrm{kcal_{th}\ mol^{-1}}}$	$\frac{-\Delta H^\circ_c(\mathrm{l})}{\mathrm{kcal_{th}\ mol^{-1}}}$	$\frac{-\Delta\{\Delta H^\circ_c(\mathrm{l})\}}{\mathrm{kcal_{th}\ mol^{-1}}}$
Cycloalkane	495.09		786.54		936.88	
		308.77		308.90		309.77
1,1-Dimethylcycloalkane	803.86		1095.44		1246.65	
		1.69		1.62		1.66
1,*cis*-2-Dimethylcycloalkane	805.55		1097.06		1248.31	
		1.06		1.42		1.54
1,*trans*-2-Dimethylcycloalkane	804.49		1095.64		1246.77	

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