Thermodynamic properties of 1,3,3-trimethylcyclopropene

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ABSTRACT

The energy of combustion of liquid 1,3,3-trimethylcyclopropene was obtained in isoperibolic calorimeter at T = 298.15 K. The saturated vapour pressures were determined by the comparative ebulliometry in the temperature range 295–310 K. The normal boiling temperature and the enthalpy of vaporization were estimated based on p-T-data. The enthalpy of vaporization was measurement by calorimetric method at T = 298.15 K. The density was determined by pycnometric method at T = 293.15 K. The formation enthalpies of the compound in liquid and gas states were determined using the obtained experimental data. The enthalpies of formation in the gaseous state for cyclopropene and its methyl-substituted derivatives were estimated by G4 method.

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1. Introduction

At present, the cyclopropene and its derivatives cause increasing interest of researchers. The ring strain energy of these compounds is significantly higher compared to other cycloolefins [1]. Electron unsaturation of the cycle is a cause low stability of these compounds and their increased tendency to various transformations. Because of this, they are widely used in organic synthesis.

The cyclopropene fragment occurs as a structural element of various natural compounds, which (like many synthetic derivatives of cyclopropene) have a wide spectrum of biological activity [2,3,4,5]. Taking into account the ability to inhibit ethylene receptors, cyclopropenes are widely used in the storage of fruits, as fungicides, regulators of growth and maturation of plants [2,3].

Experimental thermochemical studies of cyclopropene and its derivatives are an important and necessary task. In the literature there are two experimental works [6,7] devoted to the determination of combustion energies of cyclopropene compounds. The enthalpies of combustion of these compounds are determined in a calorimeter with a burner [8]. Cyclopropene was measured in [6]: $\Delta_c H_m^0(C_3H_4, g, 298 K) = (-2029.2 \pm 2.5)$ kJ·mol^{-1}, $\Delta_f H_m^0(C_3H_4, g, 298 K) = 278.65 \pm 2.5$ kJ·mol^{-1}; 1-methylcyclopropene was measured in [7]: $\Delta_c H_m^0(C_4H_6, g, 298 K) = (-2675.08 \pm 1.13)$ kJ·mol^{-1}, Δ_f

H_m^0 (C$_4$H$_6$, g, 298 K) = 243.51 ± 1.3 kJ·mol^{-1}. The purity of the 1-methylcyclopropene was controlled by NMR spectra (the impurity content less than 0.1 mol %); the purity of the cyclopropene is not given. Some preliminary thermodynamic characteristics of 1,3,3-trimethylcyclopropene (defined earlier in our laboratory) are given in [9]. In this work, we clarified the previously reported data and recommend using them in practice.

2. Experiment and results

2.1. Synthesis of sample

The sample of 1,3,3-trimethylcyclopropene (C$_6$H$_{10}$(liq)) (Fig. 1) was synthesized in the laboratory of organic synthesis of Chemical Department of Lomonosov Moscow State University by decomposing to tosylhydrasone of mesityl oxide with sodium methylate in diglyme [10].

Two samples of the substance were obtained. The first sample was purified on a preparative chromatograph, the second was purified by multiple distillation (column 80 theor. plates) and preparative chromatography (Table 1).

Samples of the substance contained unidentified impurities: the first had 0.8 wt%, the second had 0.2 wt% (g.l.c. analysis, XT-7-IC chromatograph). Purity of studied samples of 1,3,3-trimethylcyclopropene was also controlled by the analysis of the gaseous products of combustion on content of CO$_2$(g) [11]. The molar mass of 1,3,3-trimethylcyclopropene (M = 82.1434 g·mol^{-1})
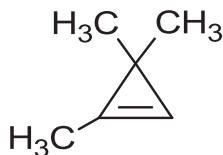
Fig. 1. 1,3,3-trimethylcyclopropene.

Table 1
Provenance and purity of liquid sample of 1,3,3-trimethylcyclopropene.

Compound	Source	PurificationMethod	Method of analysis	Final purity[a] mass fraction
Sample I C₆H₁₀	synthesized	preparative g.l.c.	analytical g.l.c. analysis CO_2(g)	0.9920 0.9996
Sample II C₆H₁₀	synthesized	distillation and preparative g.l.c.	analytical g.l.c. analysis CO_2(g)	0.9980 0.9998

[a] The standard uncertainty u is u(g.l.c.) = 0.0002 mass fraction; the combined expanded uncertainty U_c is U_c(analysis CO_2(g)) = 0.0002 mass fraction (0.95 level of confidence).

Table 2
Calorimetric determination of the vaporization enthalpy, $\Delta_v H°_m$(298.15 K), of 1,3,3-trimethylcyclopropene[a] (Molar Mass = 82.1434 g·mol⁻¹).

Experiment	q/kJ	m_{vac}/g	$\Delta_v H°_m$(298.15 K)/ (kJ·mol⁻¹)
Sample I			
1	0.028262	0.08435	27.52
2	0.028350	0.08347	27.90
3	0.027991	0.08279	27.77
Sample II			
4	0.028372	0.08419	27.68
5	0.028243	0.08408	27.59
Mean of five experiments			27.69

q is energy adsorbed in vaporization; standard uncertainty is $u(q)$ = 0.000003 kJ; m_{vac} is mass of the sample in the vacuum taking into account the loss in preparation; standard uncertainty is $u(m_{vac})$ = 0.00002 g; combined expanded uncertainty is $U_c(\Delta_v H°_m)$ = 0.19 kJ·mol⁻¹ (0.95 level of confidence);
[a] standard uncertainty u is $u(T)$ = 0.01 K.

were calculated based on relative atomic masses recommended in [12]. The density of 1,3,3-trimethylcyclopropene is ρ = 0.6898 g·cm⁻³ at T = 293.15 K. The density of sample II was determined by pycnometric method. The volume of the quartz pycnometer is 1 cm³; the combined expanded uncertainty is $U_c(\rho)$ = 0.0006 g·cm⁻³ (0.95 level of confidence) (Table S1 of Supplementary data).

2.2. Calorimetric determination of enthalpy of vaporization

The enthalpy of vaporization at T = 298.15 K, $\Delta_v H°_m$(298.15 K), was determined by calorimetric method. The heat absorbed during the vaporization of the substance was balanced by introduction of equivalent amount of electric energy into the heater of the calorimeter (R_{heater} = 49.721 ± 0.005 Ω). In each experiment, the heating continued about 900 s. The vapour pressure of the substance in calorimeter equals to saturation pressure at T = 298.15 K. For uniform evaporation over the substance in the calorimetric cell through the capillary was passed the carrier gas (nitrogen). The gas flow rate and current power were selected such that the temperature of the calorimetric cell was constant during measurement and equal to the temperature of a water thermostat (temperature 298.15 ± 0.003 K). This was controlled by the thermistor resistance ($R \sim 2$ kΩ, temperature coefficient is ~80 Ω·K⁻¹) located in the calorimeter cell. Detailed description of the device configuration and technique are

in [13]. At preparing the cell for measurement, there is some loss of substance (it are 0.00083–0.00089 g for the sample I; 0.00070–0.00076 g for the sample II). This loss is taken into account when calculating the enthalpy of vaporization. The results of five experiments for two samples of the 1,3,3-trimethylcyclopropene are shown in Table 2.

2.3. Saturation vapour pressure

For sample II the vapour pressure, p_{exp}, as a function of temperature, T_b, was determined by comparative ebulliometry in four points of the temperature range 295–310 K and the pressure range 44–82 kPa. (Table S2 of Supplementary data). The device consists of a ebulliometer for measuring the boiling temperatures, T_b, and a manometric system used for automatic control and determination of the pressure, p_{exp}, inside ebulliometric system. Detailed description of the device configuration and technique are in [14]. The boiling temperatures were measured with a platinum resistance thermometer (R_o = 50 Ω) by the potentiometer method. The volume of the test liquid is ~2.5 cm⁻³. The boiling temperature at each pressure is averages value calculated from 6 to 8 measurements. The combined expanded uncertainties are $U_c(T_b)$ = 0.01 K (0.95 level of confidence) and $U_c(p_{exp})$ = 26 Pa (0.95 level of confidence).

Experimental data are approximated by a linear equation (Fig. S1 of Supplementary data):

$$Ln(p/Pa) = A + B/T(K), \tag{1}$$

where A = 22.37 ± 0.07, B = −3439 ± 20 (r² = 0.9999).

The enthalpy of vaporization, $\Delta_v H_m$, is calculated using the Clausius-Clayperon equation:

$$\frac{dp}{dT} = \Delta_v H_m/(\Delta Z \cdot R \cdot T), \tag{2}$$

where ΔZ is the difference in the compression factors of gas and liquid, which takes into account the deviation of the vapour from ideality; R = 8.3144598 J·K⁻¹·mol⁻¹. The value ΔZ(298.15) was calculated by the equation [15]:

$$\Delta Z(298.15) = \left[1 - P_r/T_r^3\right]^{0.5}, \tag{3}$$

where $P_r = p(298.15)/P_{cr}$ и T_r = 298.15/T_{cr}. The critical parameters, P_{cr} and T_{cr}, were found by the additive method [16]. Table 3 shows the obtained thermodynamic values.

2.4. Combustion calorimetry

Detailed description of configuration of the static-bomb isoperibolic calorimeter was reported in [17]. The increase of the temperature was measured by means of copper resistance thermometer ($R_{298} \sim 50$ Ω) using bridge circuit [18], 1 K temperature change corresponds to 0.1964 Ohm change in resistance. The sensitivity of the temperature measurements was about 5·10⁻⁵ K. The volume of the calorimetric bomb was 0.270 dm³.

The burning of 1,3,3-trimethylcyclopropene was accompanied by the formation of a large amount of soot in the bomb. Completeness of combustion was obtained in only three experiments with sample I (experiments 1–3, Table 4) and three experiments with sample II (experiments 4–6, Table 4).

The energy equivalent of the calorimetric system, ε(Calor.), was determined with thermochemical standard benzoic acid (K-1 brand, D.I. Mendeleev Research Institute of Metrology) using the energy of combustion in certified conditions $\Delta_b u$ = (−26,432.5) J·g⁻¹ at T = 298.15 K (combined expanded uncertainty of $\Delta_b u$ is $U_c(\Delta_b u)$ = 1.9 J·g⁻¹; standard uncertainty of T is $u(T)$ = 0.05 K). The correction for small deviations from these conditions was calculated according to Jessup's formula [11]. The mean values

Table 3
Normal boiling temperature, $T_{n.boil}$, molar enthalpy of vaporization, $\Delta_v H°_m(298.15$ K), and difference in the compression factors of gas and liquid, $\Delta Z(298.15)$, of 1,3,3-trimethylcyclopropene.

$T_{n.boil}$[a]/K	$\Delta_v H°_m(298.15$ K)[a]/(kJ·mol^{-1})	$\Delta Z(298.15$ K)
317.04	27.7	0.9680

[a] Standard uncertainties u are $u(T_{n.boil})$ = 0.01 K and $u(\Delta_v H°_m)$ = 0.4 (kJ·mol^{-1}).

obtained for the energy equivalent with an empty bomb were ε (Calor.)$_I$ = 54,082.3 J·Ω^{-1} for experiments 1–3 (sample I) and ε (Calor.)$_{II}$ = 54,033.2 J·Ω^{-1} for experiments 4–6 (sample II), Table 4; combined expanded uncertainties are $U_c(\varepsilon$(Calor.)$_I$ = 4.2 J·$\Omega.^{-1}$ and $U_c(\varepsilon$(Calor.)$_{II}$ = 4.8 J·Ω^{-1} (both are 0.95 level of confidence). The energy contents of the final products after burning benzoic acid in the calibration experiments for the samples I and II are 66.8 J·Ω^{-1} and 65.8 J·Ω^{-1}, respectively. The energy content of the final products of combustion for samples I and II are given in Table 4; these were calculated according to [11].

In experiments with sample I, the substance (about 0.25 g) was placed in flat ampoules of plain glass, ignited by passing a current through an iron wire (Ø = 0.1 mm) at a capacitor discharge. During the combustion of an iron wire, Fe_2O_3 was formed. This was established by X-ray phase analysis. The sample II (about 0.198 g) was placed in capsules of a Terylene film ($C_{10}H_8O_4$), ignited by passing a current through a platinum wire (Ø = 0.1 mm).

Weighing was carried out on Mettler balance (Type 100 A5M, Max. Bel. 100 g); standard uncertainty is $u(m_{vac})$ = 0.02 mg. The bomb, with 1 ml of distilled water added, was charged with purified oxygen to a pressure 3.04 MPa. The initial temperature did not differ from 298.15 K by more than 0.03 K.

The combustion products were analysed for carbon dioxide by the Rossini method [11]. The content of CO_2 in the combustion products of the samples I and II of 1,3,3-trimethylcyclopropene equals to 0.9997 mass fractions. The combined expanded uncertainty of the analyses of combustion products is U_c(analysis of CO_2(g)) = 0.0002 mass fractions. For the burning of the substance, optimal combustion conditions were selected. However, out of 17 experiments performed, only in 6 experiments the substance burned out without the formation of soot and CO (Table 4). Qualitative tests for CO with indicator tubes (TU. 12.43.20-76) were negative within the limits of their sensitivity $6·10^{-6}$ g of CO. The found amount of carbon dioxide within the uncertainty corresponds to the theoretical value.

The content of HNO_3 in the solution was determined by titration of washing waters by ~0.1 mol·dm^{-3} of NaOH (aq).

The results of the determination of specific combustion energy, $\langle-\Delta_c u°\rangle$, of 1,3,3-trimethylcyclopropene (from 6 combustion experiments) are shown in Table 4.

The obtained close results of the combustion energies and gas analysis of the combustion products of the two studied samples suggest that the unidentified impurities correspond to isomers,

Table 4
Combustion energy of 1,3,3-trimethylcyclopropene at liquid state at T = 298.15 K. ([a]Molar Mass = 82.1434 g·mol^{-1}; $p°$ = 101.3 kPa; ρ[b] = 0.6898 g·cm^{-3}).

Sample	I			II		
Experiment	1	2	3	4	5	6
m/g	0.24180	0.25243	0.26145	0.19771	0.19922	0.19834
m (Fe)/g	0.00372	0.00405	0.00450	–	–	–
m (f)/g	–	–	–	0.03414	0.01082	0.01236
$\Delta R_{corr}/\Omega$	0.213819	0.223295	0.231266	0.189032	0.180528	0.180323
ε_f(Cont.)/J·Ω^{-1}	67.3	67.3	67.5	66.5	66.2	66.2
$-\Delta U$(IBP)/J	11578.2	12091.3	12523.0	10226.6	9766.5	9755.4
ΔU(Fe)/J	27.3	29.7	33.0	–	–	–
ΔU(f)/J	–	–	–	782.8	248.1	283.4
ΔU(HNO_3)/J	5.6	5.6	5.1	0.8	0.8	0.8
$\Delta U_{\sum}$/J	3.3	3.5	3.6	3.3	2.8	2.9
$(-\Delta_c u°)$/(J·g^{-1})[c]	47733.7	47745.9	47738.8	47745.2	47760.3	47737.7
$(-\Delta_c \bar{u}°)$/(J·g^{-1})[d]	$(-\Delta_c \bar{u}°)_I$ = 47739.5			$(-\Delta_c°)_{II}$ = 47747.7		
Mean $(-\Delta_c u°)$/(J·g^{-1})[e]	47743.6 ± 9.8					
$m(CO_{2expt})/m(CO_{2theor})$[f]	0.9994	0.9999	0.9995	0.9998	0.9999	0.9997
Mean[g] 0.9997 ± 0.0002						

m is mass of the sample in the vacuum; standard uncertainty is $u(m_{vac})$ = 0.02 mg.
m(Fe) is mass of Fe-wire in the vacuum, ρ = 7.874 g·cm^{-3}[19];
m(f) is mass of Terylene-film ($C_{10}H_8O_4$) in the vacuum, ρ = 1.38 g·cm^{-3}[20];
ΔR_{corr} is the increase of the thermometer resistance corrected for heat exchange (1 K temperature change corresponds to 0.1964 Ohm change in resistance); standard uncertainty is $u(\Delta R_{corr})$ = 1 × 10^{-5} Ω;
ε_f(Cont.) is the energy equivalent of contents bomb in the final state; the combined expanded uncertainty is $U_c(\varepsilon_f$(Cont.)) = 0.1 J·Ω^{-1} (0.95 level of confidence);
$-\Delta U$(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions, ε(Calor.)$_I$ = 54082.3 J·Ω^{-1}, ε(Calor.)$_{II}$ = 54033.2 J·Ω^{-1}; the combined expanded uncertainties are $U_c(\Delta U$ (IBP)) = 4.2 J and 4.8 J, respectively (0.95 level of confidence);
ΔU(Fe) is the correction for the energy combustion Fe; $\Delta_c u°$(Fe) = (−7328 ± 36) J·g^{-1}, which is calculated from the value $\Delta_f H°(Fe_2O_3)$ =(−822.2 ± 4.0) kJ·mol^{-1} [21]. The combined expanded uncertainty is $U_c(\Delta U$(Fe)) = 0.05 J (0.95 level of confidence);
ΔU(f) is the correction for the energy combustion of film. The energy of combustion of Terylene-film ($C_{10}H_8O_4$) is $\Delta_c u°$ = (−22927.9 ± 6.3) J·g^{-1} [22]; the combined expanded uncertainty is $U_c(\Delta U$(f)) = 0.1 J (0.95 level of confidence);
ΔU(HNO_3) is the correction for the energy formation of solution HNO_3(aq) from N_2(g), O_2(g) and H_2O(liq) (based on −59.5 kJ·mol^{-1} the molar energy of formation of aqueous nitric acid [21,23]); the combined expanded uncertainty is $U_c(\Delta U$(HNO_3)) = 0.002 J (0.95 level of confidence);
$\Delta U_{\sum}$ is the correction to standard state [11]; the standard uncertainty is $u(\Delta U_{\sum})$ = 0.08 J.
[a] Standard uncertainties u are u(Molar Mass) = 0.0002 g·mol^{-1}, $u(p°)$ = 0.5 kPa, (T) = 0.01 K.
[b] Combined expanded uncertainty is $U_c(\rho)$ = 0.0006 g·cm^{-3} (0.95 level of confidence);
[c] $(-\Delta_c u°)$ is the standard specific energy of combustion.
[d] $(-\Delta_c \bar{u}°)$ are the mean values of specific energy of combustion of the samples I and II.
[e] Mean $(-\Delta_c u°)$ is mean value of the specific energy of combustion from data for tow samples; the combined expanded uncertainty is $U_c(-\Delta_c u°)$ = 9.8 J·g^{-1} (0.95 level of confidence).
[f] $(mCO_{2expt})/(mCO_{2theor})$ is the ratio of the mass of CO_2 determined experimentally to that calculated theoretically for the composition of the substance and film ($C_{10}H_8O_4$).
[g] The mean value $(mCO_{2expt})/(mCO_{2theor})$ for the two samples; the combined expanded uncertainty is $U_c((mCO_{2expt})(mCO_{2theor}))$ = 2 × 10^{-4} g (0.95 level of confidence).

the influence of which on the values of the energy of combustion and gas analysis are outside the measurement errors.
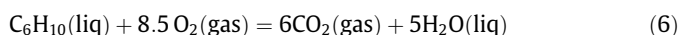
The change of internal energy for the isothermal bomb process $\Delta U(\text{IBP})$ was calculated in accordance with [11]:

$$-\Delta U(\text{IBP}) = [\varepsilon(\text{Calor.}) + \varepsilon_{\text{f}}(\text{Cont.})]\Delta R_{\text{corr}} \tag{4}$$

The value, $(-\Delta_c u°)$, was calculated based on the sample mass using the following formula:

$$(-\Delta_c u°) = \left\{ -\Delta U(\text{IBP}) - \Delta U(\text{Fe}) - \Delta U(f) - \Delta U(\text{HNO}_3) - -\Delta U_{\sum}(st) \right\} \cdot m^{-1} \tag{5}$$

and was attributed to the combustion reaction of this substance:

$$C_6H_{10}(\text{liq}) + 8.5\,O_2(\text{gas}) = 6CO_2(\text{gas}) + 5H_2O(\text{liq}) \tag{6}$$

Analysis of the obtained values of the mean specific combustion energies of samples I, $(-\Delta_c \bar{u}°)_I$, and II, $(-\Delta_c \bar{u}°)_{II}$, of 1,3,3-trimethylcyclopropene (with using t-criterion) showed that their difference is insignificant. Therefore, the results of the definitions $(-\Delta_c \bar{u}°)$ of both samples we processed together [24]. Calculation of t-criterion was carried out according to the formula:

$$t = \frac{\left(\Delta_c \bar{u}^o\right)_I - \left(\Delta_c \bar{u}^o\right)_{II}}{\sqrt{\bar{S^2}}} \cdot \sqrt{\frac{n_I \cdot n_{II}}{n_I + n_{II}}} \tag{7}$$

where n_I and n_{II} are the number of experiments in the series;

$\bar{S}2 = \frac{(n_I - 1)\cdot S_I^2 + (n_{II} - 1)\cdot S_{II}^2}{n_I + n_{II} - 2} = 86.72$ is weighted average dispersion;
$S_I^2 = 85.02$ and $S_{II}^2 = 265.01$ are dispersions of each series of measurements;
$(-\Delta_c \bar{u}°)_I = 47739.5$ J·g^{-1} and $(-\Delta_c \bar{u}°)_{II} = 47747.7$ J·g^{-1}.

The calculation of the t–criterion for Eq.(7) for 6 experiments gives the value $t = 0.77$, which is less than the table value $t_{0.05}(4) = 2.78$, i.e., the observed difference in the values $(-\Delta_c \bar{u}°)_I$ and $(-\Delta_c \bar{u}°)_{II}$ for samples I and II of the 1,3,3-trimethylcyclopropene is insignificant. As a result, the average value of the standard specific energy of combustion in liquid state of 1,3,3-trimethylcyclopropene is $(-\Delta_c u°) = 47743.6$ J·g^{-1}; the combined expanded uncertainty is $U_c(-\Delta_c u°) = 9.8$ J·g^{-1}.

2.5. Energy and enthalpy of combustion in liquid state at T = 298.15 K

The standard molar energy of combustion was received equal to $(-\Delta_c U_m°) = 3921.8$ kJ·mol^{-1}. The combined expanded uncertainty is $U_c(-\Delta_c U_m°) = 0.8$ kJ·mol^{-1}.

The standard molar enthalpy of combustion, $\Delta_c H°_m$ (liq), is found by the formula:

$$\Delta_c H_m^o = \Delta_c U_m^o + \Delta_n \cdot RT, \tag{8}$$

where $\Delta n = -2.5$ mol is the difference in the number of moles of gas after and before the burning of the 1,3,3-trimethylcyclopropene (according to reaction (6)); $R = 8.3144598$ J·K^{-1}·mol^{-1}; $T = 298.15$ K.

The value of $\Delta_c H_m°$ is equal to (-3928.0) kJ·mol^{-1}. The combined uncertainty $U_c(\Delta_c H_m°)$ equal to 1.0 kJ·mol^{-1}. The calculation of $U_c(\Delta_c H_m°)$ included the uncertainty of calibration calorimeter (0.01%), the uncertainty in determining the combustion energy of benzoic acid (0.01%) and the uncertainty in determining of the substance (0.02%).

2.6. Enthalpy formation of 1,3,3-trimethylcyclopropene in liquid and gas states at T = 298.15 K

The standard molar enthalpy of formation, $\Delta_f H°_m(\text{liq})$, in liquid state at $T = 298.15$ K here calculated corresponds to reaction (6) using $\Delta_c H°_m$ of the 1,3,3-trimethylcyclopropene, and standard molar enthalpies of formation of $\Delta_f H°_m CO_2(g) = (-393.51 \pm 0.13)$ kJ·mol^{-1} and $\Delta_f H°_m H_2O(\text{liq}) = (-285.83 \pm 0.04)$ kJ·mol^{-1} recommended by CODATA [23].

The standard molar enthalpy of formation, $\Delta_f H°_m(g)$, in gas state at $T = 298.15$ K was calculated using enthalpy of vaporization (Table 2). The obtained thermodynamic characteristics are given in the Table 5.

As well, the enthalpies of formation, $\Delta_f H°_m(g)$, for cyclopropene and its methyl-substituted derivatives were calculated by G4 method [25] from atomization and isodesmic reactions (Tables S3–S5 of Supplementary data). The calculations were performed using the Gaussian 16 package of programs [26]. The results are given in Table 6.

3. Discussion

The experimental enthalpies of formation in the gas phase at 298.15 K for cyclopropene and two its methyl-substituted derivatives are compared with those calculated by quantum-chemical methods in Table 6. It can be seen that the calculated values for 1,3,3-trimethylcyclopropene are higher than the experimental one by 6.1% for the atomization reaction and by 4.5% for the isodesmic reactions. This discrepancy exceeds the usually expected error of calculated G4 values, it should be noted that the $\Delta_f H_m^o(g)$ values for cyclic and polycyclic hydrocarbons obtained by G4 method may be subject to relatively large errors. Recently it was noted that the G4 enthalpies of formation of adamantane calculated both from the atomization reaction and from isodesmic reactions are underestimated from (7 to 10) kJ·mol^{-1} [27].

Some support for our experimental value may be obtained from estimation of contribution of CH_3 group in the enthalpy of formation of methyl-substituted cyclopropenes and cyclopropanes (Fig. 2). Assuming that thermodynamic properties can be calculated as the sum of contributions from all structural units, the enthalpic increment for the methyl group, $\Delta H[\text{C–C(H)3}](g)$, was estimated using the experimental and calculated values in the series of methyl derivatives of cyclopropene and cyclopropane (Fig. 2).

Comparison values of these increments in the series of methyl derivatives of cyclopropane found from data from both methods gives almost the similar result. The scatters when using experimental values are (1.5–3.1) kJ·mol^{-1}, when using calculated values are (3.2–6.4) kJ·mol^{-1}.

A similar pattern is observed in the series of well-studied group of methyl-substituted benzenes (Table S6 of Supplementary data), where each CH_3 group decreases the enthalpy of formation by about 33 kJ·mol^{-1} in going from benzene to 1,2,4,5-tetramethylbenzene.

A different picture is observed for cyclopropenes (Fig. 2). The experimental data, including our experimental value for 1,3,3-
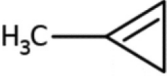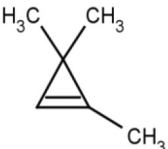
Table 5
Standard enthalpy of combustion, $\Delta_c H°_m$, and formation, $\Delta_f H°_m$, of 1,3,3-trimethyl-cyclopropene in liquid and gaseous state, and enthalpy of vaporization, $\Delta_v H°_m$, at $T = 298.15$ K, (kJ·mol^{-1}).[a]

$\Delta_c H°_m/S$	$\Delta_f H°_m(\text{liq})/S$	$\Delta_v H°_m/S$	$\Delta_f H°_m(g)/S$
−3928.0	137.8	27.69	165.4

[a] Combined expanded uncertainties U_c are $U_c(\Delta_c H_m^o) = 1.0$ kJ·mol^{-1}, $U_c(\Delta_f H_m^o(\text{liq}))$ = 1.3 kJ·mol^{-1}, $U_c(\Delta_v H_m^o) = 0.19$ kJ·mol^{-1}, $U_c(\Delta_f H_m^o(g)) = 1.4$ kJ·mol^{-1} (all are 0.95 level of confidence).

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Table 6
The experimental and calculated enthalpies of formation of cyclopropene and its methyl-substituted derivatives at 298.15 K.

Compound	$\Delta_f H°_m(g)/$ kJ·mol^{-1}				
	Exp.	calculation			
		Isodesmic reaction	(Exp. – isodesmic reaction)	Atomization reaction	(Exp. – atomization reaction)
(triangle structure)	278.6 ± 2.5[6] 283.6 ± 0.5 [28]	284.1	−5.5–0.5	284.7	−6.1 −1.1
H₃C— (cyclopropene structure)	243.5 ± 1.3 [7]	239.4	4.1	240.9	2.6
H₃C CH₃ (dimethyl cyclopropene structure) CH₃	165.4 ± 1.4 [This work]	173.0	−7.6	175.8	−10.4
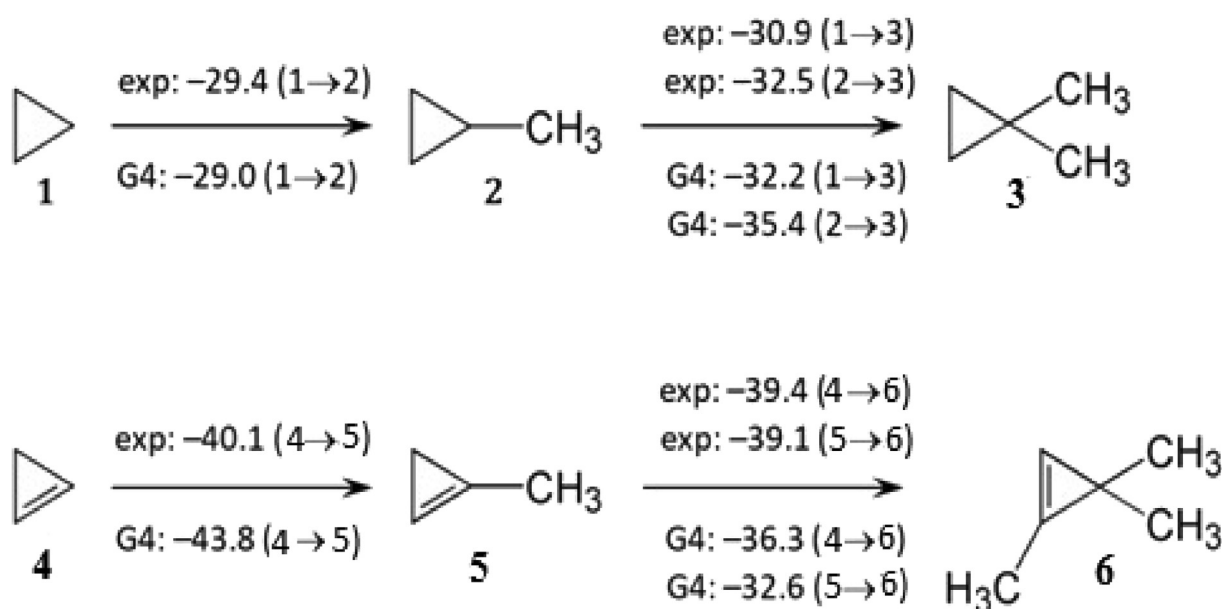
Fig. 2. Contribution of CH$_3$ group (kJ·mol^{-1}) in the enthalpy of formation of methyl-substituted cyclopropanes and cyclopropenes determined as the difference in the corresponding enthalpies of formation. The following values of enthalpy of formation are used (in kJ·mol^{-1}): 53.6 for **1** [28], 24.3 for **2** [28], −8.2 for **3** [29]; the values for compounds **4–6** are taken from Table 6.

trimethylcyclopropene, give practically the same contribution of CH$_3$ group (about −39.3 kJ·mol^{-1}), whereas the discrepancy in calculated values reaches (7.5–11.2) kJ·mol^{-1}. Thus, it can be suggested that the results of G4 calculations are insufficiently accurate for cyclopropenes.

4. Conclusions

Although the obtained experimental enthalpy of formation in a gaseous state is lower than the calculated value by 10.4 kJ mol^{-1} (6.1%) atomization reaction and by 7.6 kJ mol^{-1} (4.5%) isodesmic reactions, it cannot be ruled out that the results of G4 calculations are insufficiently accurate for cyclopropenes. This suggestion is supported by estimating the change of methyl group contribution in the enthalpy of formation of cyclopropenes. We hope that this contradiction will be solved by higher-level quantum chemical calculations.

Declaration of Competing Interest

We agree with the comments of the editor and reviewers. Thank them.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jct.2020.106240.

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