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Thermochimica Acta 408 (2003) 115–121

thermochimica acta

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Short communication

Thermodynamics of sublimation of cubane: natural anomaly or experimental error?[☆]

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Received 17 April 2003; received in revised form 17 April 2003; accepted 2 June 2003

Abstract

An analysis of the available experimental values of the enthalpy of sublimation of monocyclic, bicyclic, and 'cage' hydrocarbons is performed. Based on the results of this analysis, the value of the enthalpy of sublimation for cubane is found to be anomalous in the series of structurally related hydrocarbons. The potential cause of this anomaly, as well as its impact on the value of the enthalpy of formation of cubane in the gas state at 298.15 K are discussed with emphasis on the reliability of the value, which is used as a key reference value for force field and quantum–chemical computations.

Keywords: Cubane; Enthalpy; Formation; Sublimation; Thermodynamics

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1. Introduction

Thermophysical and thermochemical properties of cubane are widely used as benchmarks for the development and testing of various prediction methods. Due to the presence of four-membered rings, its carbon structure is highly strained, with the valence angles deviating greatly from the tetrahedral values. Besides, the high symmetry of the cubane molecule reduces the number of parameters necessary for calculations, which facilitates both the calculation of its structure and properties and the derivation of empirical parameters. The enthalpy of formation of gaseous cubane $\Delta_f H^\circ(\mathrm{g},\ 298.15\,\mathrm{K}) = (622.2 \pm 4.2)\,\mathrm{kJ\,mol^{-1}}$ reported by Kybett et al. [1] was used in the development of the MM3 force field [2] and as a reference value for the assessment of capabilities of modern quantum chemistry methods (Table 1). Cubane is also used as a reference compound for the calculation of enthalpies of formation of other highly strained hydrocarbons in homodesmic or isodesmic reactions.

The purpose of this short communication is to show the anomalous thermodynamic characteristics of sublimation of cubane, which are difficult to attribute to its strained carbon structure and to raise awareness of this anomaly in the computational chemistry community. We also hope that the results of our analysis will serve as an encouragement to experimentalists to initiate new thermochemical studies of the sublimation of cubane in order to confirm or reject its apparently anomalous behavior.

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doi:10.1016/S0040-6031(03)00318-6

Table 1
Experimental and recently calculated values of $\Delta_f H^\circ$ (g, 298.15 K) of cubane

Method	Value	Reference
Experiment	622.2	[1]
G2 (bond separation)	602.9	[3]
G3(MP2) (isomerization)	610.9	[4]

2. Results and discussion

The enthalpy of formation of gaseous cubane [1] was obtained more than 35 years ago and is based on experimental values of the enthalpy of formation of crystalline cubane ($541.8 \pm 3.3\,\mathrm{kJ\,mol^{-1}}$) and the enthalpy of sublimation derived from saturated vapor pressures measured as a function of temperature by the Knudsen method in the temperature range 239–262 K ($\log P(\mathrm{torr}) = 14.0 - (4190/T)$ or $\ln P(\mathrm{Pa}) = 37.1 - (9648/T)$).

For the purpose of our analysis, we compare the value of the enthalpy of sublimation derived from the vapor pressure data [1] for cubane with the corresponding values for other cage hydrocarbons [5–7] such as heptacyclo[6.6.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane (HCTD), pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (PCU), and adamantane (Table 2). Though Kybett et al. [1] associate the value $80.2 \pm 1.7\,\mathrm{kJ\,mol^{-1}}$ with $T = 298.15$ K, this value actually corresponds to the mean temperature of the temperature range of the measurements, 250.5 K. Based on available heat capacity data for gaseous [8] and crystalline [9] cubane, we adjusted it to $T = 298.15$ K: $\Delta_{\mathrm{sub}}H^\circ(298.15\,\mathrm{K}) = 79.1 \pm 1.7\,\mathrm{kJ\,mol^{-1}}$. The cage hydrocarbons selected for the comparison have only CH– and CH_2– groups in their molecules. The values of the enthalpies of sublimation for the compounds selected for comparison are expected to be reliable since they are determined from both direct calorimetric studies and vapor pressure measurements. Fig. 1 illustrates a correlation between enthalpies of sublimation of the selected cage hydrocarbons as well as those of bicyclo[2.2.2]octane and cyclododecane (the only other hydrocarbons from Table 2 existing in the crystalline state at 298.15 K) and their molar masses. It appears that cubane shows anomalous behavior in comparison with the other selected hydrocarbons.

This anomalous behavior becomes yet clearer if we take into account solid-to-solid transitions occurring below $T = 298.15$ K. Indeed, cubane exists in its low-temperature crystalline state at $T = 298.15$ K and shows a solid-to-solid transition at $T = 394.02$ K [9]. Since for pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane and adamantane similar solid-to-solid transitions occur below 298.15 K, for appropriate comparison these enthalpies of the solid-to-solid transitions (adjusted to $T = 298.15$ K) were added to $\Delta_{\mathrm{sub}}H^\circ(298.15\,\mathrm{K})$ to obtain the enthalpies of sublimation of these compounds for a hypothetical rigid crystal at 298.15 K. Analogous corrections for solid-to-solid and solid-to-liquid transitions occurring below 298.15 K were made for relevant cyclic and bicyclic hydrocarbons by use of the values tabulated in Table 2. The results of the correlation of the enthalpies of sublimation from the rigid crystalline state at $T = 298.15$ K and molar masses for cyclic, bicyclic and cage hydrocarbons are shown in Fig. 2.

In our view, it is difficult to find an explanation of how this anomaly might be ‘natural’. Even though the molecule of cubane is extremely strained, that should have an impact only on intramolecular properties. Since the enthalpy of sublimation is related to intermolecular interactions, it is unlikely that the high molecular strain energy could lead to an anomalous value of the enthalpy of sublimation. Cubane is also a very dense compound in its crystalline form ($1269\,\mathrm{kg\,m^{-3}}$). This could be due to a closer molecular packing and could be associated with the increased enthalpy of sublimation. However, high density of heptacyclo[6.6.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane ($1242\,\mathrm{kg\,m^{-3}}$) does not exhibit an anomalous value of enthalpy of sublimation for this compound.

We tried to extend the list of saturated hydrocarbons consisting of CH– and CH_2– groups (cyclic, polycyclic, and cage) included in our analysis. Unfortunately, there are very few hydrocarbons existing in the crystalline state at $T = 298.15$ K for which enthalpies of sublimation are known. Absence of information about phase transitions in the condensed state makes the nature of their crystalline state (rigid or plastic crystal) questionable, and values of enthalpies of sublimation from the rigid crystal state have uncertainties to $10\,\mathrm{kJ\,mol^{-1}}$ or even higher.

Based on the information in Table 2, and assuming an additive nature for the enthalpy of sublimation

Table 2
Enthalpies of sublimation of saturated cyclic hydrocarbons and auxiliary data[a,b]

Compound	State[c]	Formula	M (g mol^{-1})	D (kg m^{-3})	$\Delta_{vap}H°$ ($\Delta_{sub}H°$)[d] (kJ mol^{-1})	T_{tr} (K)	$\Delta_{tr}H°$ (kJ mol^{-1})	$\Delta_{tr}C_p$ (J K^{-1} mol^{-1})	$\Delta_{sub}H°$[e] (kJ mol^{-1})
Cubane[f]	rc	C_8H_8	104.15	1269[g]	79.1	394.02[h]			79.1
						404.9[h]			
Adamantane[i]	sc	$C_{10}H_{16}$	136.23		58.76	208.7[j]	3.376[j]	8.2	(62.9)
						543.2			
PCU[k]	sc	$C_{11}H_{14}$	146.23		55.85	164.4	4.861	36.8	(65.6)
						475.8			
HCTD[l]	rc	$C_{14}H_{16}$	184.28	1242	79.29	355			79.29
						440			
Bicyclo[2.2.2]octane	sc	C_8H_{14}	110.20		47.62[m]	164.26	4.55	3.8	(53)
						447.44			
cis-Perhydroindane	l	C_9H_{16}	124.22		46.12[m]	182.29	8.27	37.5	
						184.9	0.39	0.8	
						236.49	1.39	13.1	(61)
trans-Perhydroindane	l	C_9H_{16}	124.22		44.76[m]	213.87	10.91	44.6	(59)
cis-Decalin	l	$C_{10}H_{18}$	138.25		50.1[m]	216.1	2.14	14.0	
						230.19	9.49	25.8	(65)
trans-Decalin	l	$C_{10}H_{18}$	138.25		48.5[m]	242.79	14.41	34.5	(65)
Cyclohexane	l	C_6H_{12}	84.16		33.04	186.09	6.74	14.0	
						279.81	2.68	14.0	(44)
Cycloheptane	l	C_7H_{14}	98.19		38.53[m]	134.81	4.97	30.8	
						198.16	0.29	0.0	
						212.41	0.45	0.0	
						265.12	1.89	19.0	(52)
Cyclooctane	l	C_8H_{16}	112.21		43.35[m]	166.51	6.31	35.0	
						183.81	0.48	0.0	
						287.91	2.41	15.0	(57)
Cyclododecane	sc	$C_{12}H_{24}$	168.32		76.1[m,n]	199[o]	0.6[o]	0.0	(77)
						333.8[o]			

$\Delta_{vap}H°$ ($\Delta_{sub}H°$) denotes experimental enthalpy of vaporization or sublimation. T_{tr}, $\Delta_{tr}H°$, and $\Delta_{tr}C_p$ are temperature, enthalpy, and heat capacity changes of phase transitions in condensed state, including fusion.

[a] All values are for $T = 298.15$ K, except T_{tr} and $\Delta_{tr}H°$.

[b] Values are from [8], unless otherwise stated. Only information necessary for the discussion is included.

[c] rc: rigid crystal, sc: "soft" crystal (higher-temperature modifications), l: liquid.

[d] Enthalpy of vaporization (sublimation) from the condensed state stable at $T = 298.15$ K.

[e] $\Delta_{sub}H°$ are enthalpies of sublimation from the rigid crystal state, either real or hypothetical (in parentheses), at $T = 298.15$ K.

[f] [1].

[g] [10].

[h] [9].

[i] [7].

[j] [11].

[k] [6].

[l] [5].

[m] Derived from vapor pressure.

[n] [12,13].

[o] [14].

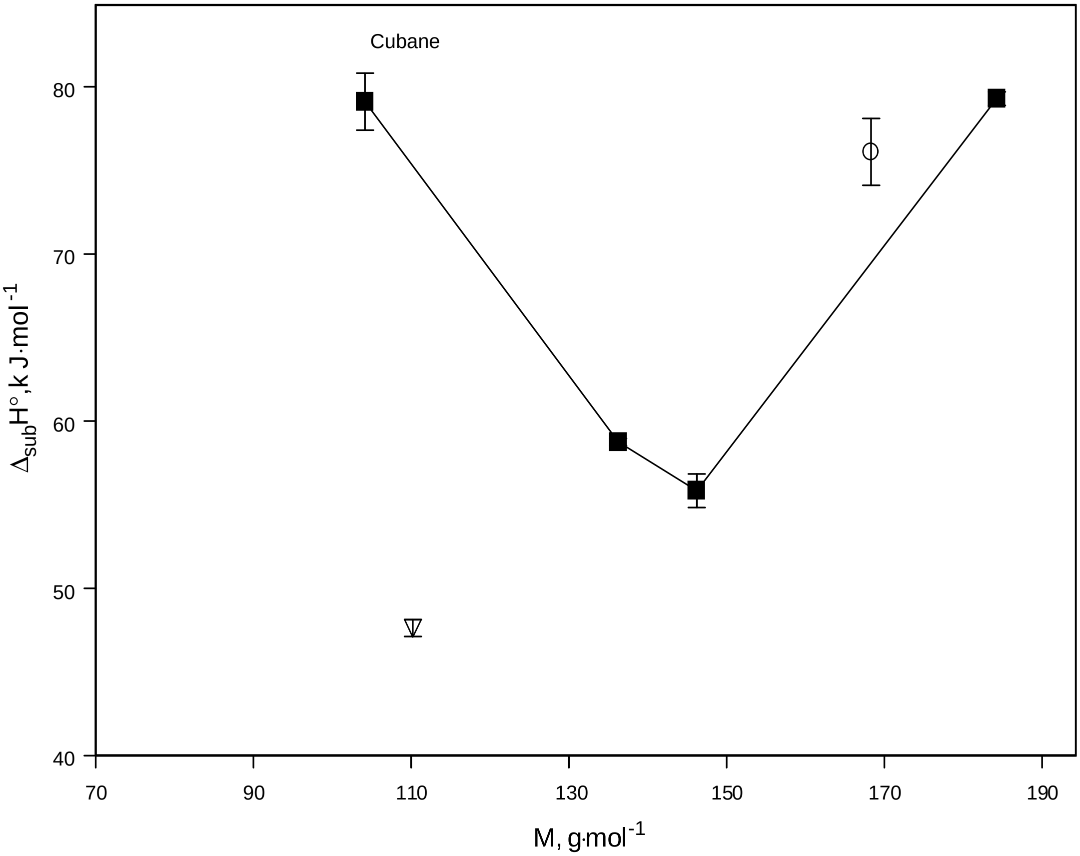

Fig. 1. Enthalpies of sublimation of saturated hydrocarbons from the crystalline state stable at $T = 298.15$ K. Cage hydrocarbons (■), bicyclic hydrocarbons (▽), monocyclic hydrocarbons (○). Connecting lines are given for convenience. Error bars represent experimental uncertainties. In cases where no error bars are given experimental uncertainties are smaller than the size of the symbols used to designate experimental values.

within a family of saturated cyclic hydrocarbons, we determined group contributions for CH_2– (6.86 ± 0.26 kJ mol^{-1}) and CH– (5.52 ± 0.41 kJ mol^{-1}). Calculated and experimental data for the enthalpy of sublimation are compared in Table 3. The differences between the calculated and experimental enthalpies of sublimation for most of the compounds are within the sum of the experimental and calculated uncertainties. However, this difference for cubane is very high (~35 kJ mol^{-1}), and is much greater than the sum of the estimated uncertainties of the experimental and calculated data. The value of the enthalpy of sublimation of cubane calculated by the atom-atom potential method (62.8 kJ mol^{-1}) [15] is also much smaller than the reported experimental value. Analysis of the data used for parametrization [16] of the force field [15] suggests to us possible overestimation of the calculated value. The values of the heats of sublimation at 0 K for pentane, hexane, and octane used for the parametrization [16] (66.48, 80.83, and 106.23 kJ mol^{-1}, respectively) are more than 1.5 times greater than the currently recommended values [17], which are traceable to primary experimental data (42.05 ± 1.67, 50.58 ± 2.09, and 66.44 ± 2.09 kJ mol^{-1}, respectively).

It is difficult to analyze the reliability of the reported experimental value of the enthalpy of sublimation of cubane [1] since neither the primary experimental vapor pressure data nor the details of experimental procedure were reported. Even though the vapor pressure

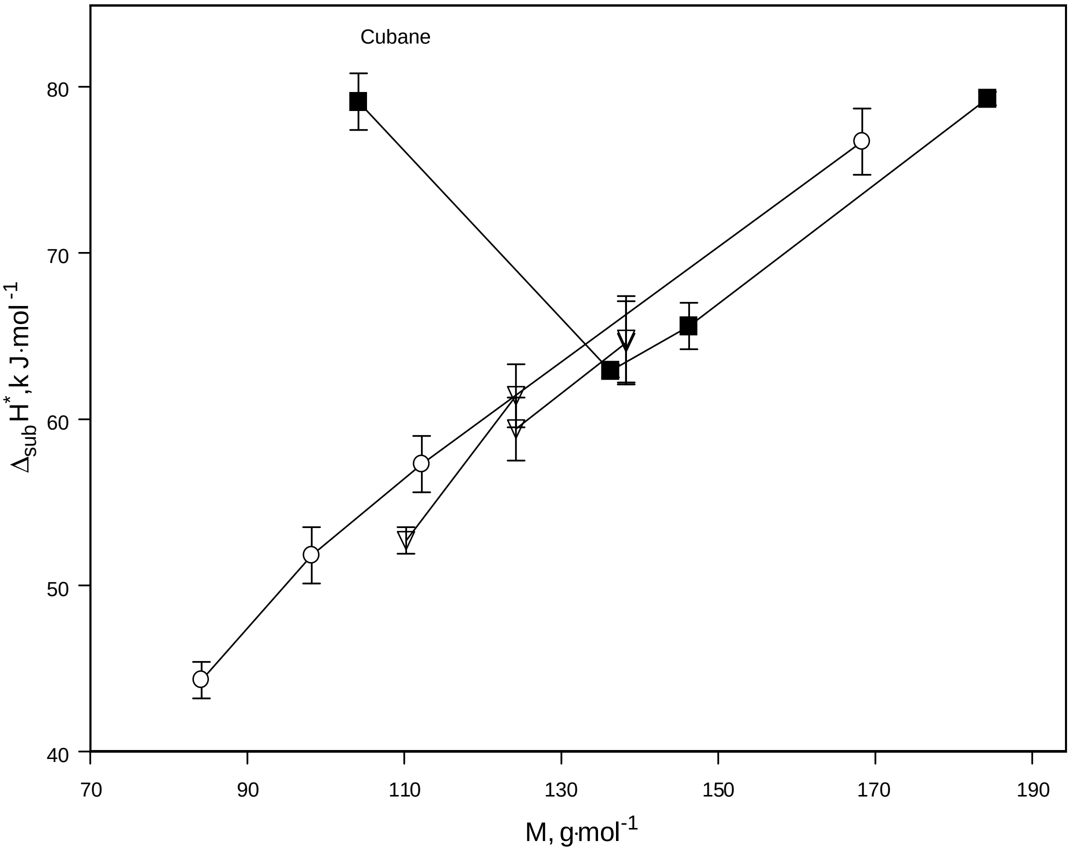

Fig. 2. Relation of enthalpies of sublimation of saturated hydrocarbons from the rigid crystal state at $T = 298.15$ K to their molar masses. Cage hydrocarbons (■), bicyclic hydrocarbons (▽), monocyclic hydrocarbons (○). Connecting lines are given for convenience. Error bars represent experimental uncertainties. In cases where no error bars are given experimental uncertainties are smaller than the size of the symbols used to designate experimental values.

range (0.04–1.37 Pa) is within the limits of the measurements using the Knudsen technique, this method has to be applied with care related to the sample purity, cell calibration, and experimental procedure [18]. For example, cyclotetradecane exists in the rigid crystalline state at 298.15 K [14]. It has been characterized with three values of the enthalpy of sublimation: 89 kJ mol^{-1} [19], 98 kJ mol^{-1}[20], and 134 kJ mol^{-1} [21]. That is why cyclotetradecane was not included in our analysis. Because of this inconsistency, the enthalpy of sublimation of cyclotetradecane was not used in the regression to obtain the group contributions for CH– and CH_2– groups. However the calculated value (96.0 kJ mol^{-1}) is in very good agreement with the most recent experimental value, 98 kJ mol^{-1} [20], and closely consistent with the earlier reported value of 89 kJ mol^{-1} [19] within the sum of the uncertainties of experimental and calculated values. The value of 134 kJ mol^{-1} [21], derived for the enthalpy of sublimation of cyclotetradecane from the vapor pressure data determined with the Knudsen method, seems to be greatly overestimated. Notably, this value appears to be traceable to the same laboratory where the vapor pressure of cubane was determined leading to the anomalous value of its enthalpy of sublimation [1].

As to the enthalpy of formation of crystalline cubane [1], 541.8 kJ mol^{-1} (129.5 kcal mol^{-1}), it is based on the standard internal energy of combustion, $\Delta_c E^\circ = -4828.3$ kJ mol^{-1} (-1154.0 kcal mol^{-1}) corrected for the formation of a “small amount of

Table 3
Determination of the contributions of CH_2– and CH– groups to enthalpies of sublimation from the rigid crystal state

Compound	Number of groups		$\Delta_{sub}H^{\circ}$ [a] (kJ mol^{-1})		|Experimental − calculated| [b] (kJ mol^{-1})	Uncertainties [c] (kJ mol^{-1})
	CH–	CH_2–	Experimental	Calculated		
Cubane[d]	8	0	79.1	44.1	35.0	5.0
Adamantane	4	6	62.9	63.2	0.3	3.6
PCU	8	3	65.6	64.7	0.9	5.5
HCTD	12	2	79.3	79.9	0.6	5.8
Bicyclo[2.2.2]octane	2	6	52.7	52.2	0.5	3.2
cis-Perhydroindane	2	7	61.4	59.0	2.4	4.6
trans-Perhydroindane	2	7	59.4	59.0	0.4	4.6
cis-Decalin	2	8	64.6	65.9	1.3	5.4
trans-Decalin	2	8	64.8	65.9	1.1	5.5
Cyclohexane	0	6	44.3	41.2	3.1	2.7
Cycloheptane	0	7	51.8	48.0	3.8	3.5
Cyclooctane	0	8	57.3	54.9	2.4	3.8
Cyclododecane	0	12	76.7	82.3	5.6	5.1
Cyclotetradecane[d]	0	14	89.3[e]	96.0	6.7	4.0
			98.3[f]		2.3	5.3
			134[g]		38	5.1

[a] $\Delta_{sub}H^{\circ}$, at $T = 298.15$ K.

[b] Absolute value of the difference between experimental and calculated enthalpy of sublimation.

[c] Sum of uncertainties of experimental and calculated values.

[d] Not used in regression.

[e] [19].

[f] [20].

[g] [21].

carbon" contained in the calorimetric bomb upon completion of the measurement process. Based on this information, it is not possible to substantiate the value for the correction introduced. Moreover, since the original value for the standard internal energy not corrected for incomplete combustion is reported to be $\Delta_c E^{\circ} = -4836.7\,\text{kJ mol}^{-1}$ ($-1156.0\,\text{kcal mol}^{-1}$), it appears that the sign of the correction is erroneous. Unfortunately, there is no other independent experimental determination of the enthalpy of formation of crystalline cubane available. The enthalpies of combustion have also been experimentally determined for two cubane derivatives in the crystalline state [22,23]. However, taking into account the large uncertainty of additional strain caused by the substituents, it is impossible to use these data to validate the reported value of the enthalpy of combustion for cubane.

We hope that our analysis will motivate experimentalists to undertake new studies of the energetics of cubane in order to provide better insight into the nature of the anomaly discussed here. We also hope that the results of this analysis will serve as a warning against indiscriminate use of the available thermodynamic data for cubane as key reference data for molecular mechanical and ab initio calculations.

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