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The thermodynamic properties of 1-bromoadamantane in the gaseous state

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Abstract

The saturated vapour pressure over two crystalline phases (crI and crII) of 1-bromoadamantane in the temperature range from 288 to 323 K was measured by the integral Knudsen effusion method with the use of a modified effusion cell with an enlarged surface of sublimation. The temperature dependences of p_{sat} are the following:

for crII between $T = 288.4$ and 309.9 K:

$$\ln\{p_{\mathrm{sat}}(\mathrm{crII})\,(\mathrm{Pa})\} = (30.33 \pm 0.44) - (8608 \pm 137) \cdot (T(\mathrm{K}))^{-1},$$

for crI from 309.9 to 323.0 K:

$$\ln\{p_{\mathrm{sat}}(\mathrm{crI})\,(\mathrm{Pa})\} = (27.07 \pm 0.81) - (7600 \pm 252) \cdot (T(\mathrm{K}))^{-1}.$$

The sublimation enthalpy for the compound at $T = 303.0$ K was measured in a differential heat-conducting microcalorimeter of the Calvet type, $\Delta_{\mathrm{sub}}H^{\circ}_{\mathrm{m}}(303.0\,\mathrm{K}) = 71.77 \pm 0.31\,\mathrm{kJ\,mol^{-1}}$, which agrees with the value obtained by the effusion measurements, $\Delta_{\mathrm{sub}}H^{\circ}_{\mathrm{m}}(298.1\,\mathrm{K}) = 71.6 \pm 1.1\,\mathrm{kJ\,mol^{-1}}$, within the experimental errors. The molar thermodynamic functions of 1-bromoadamantane in the ideal gaseous state were calculated by the statistical thermodynamic method. The complete set of the fundamentals necessary for the above calculations was made up from the experimental IR and Raman spectral data and the results of DFT calculations (B3LYP/6-31G*). The enthalpy of formation for 1-bromoadamantane was evaluated in terms of three different approaches. The thermodynamic analysis of some reactions with 1-bromoadamantane was performed.

Keywords: 1-Bromoadamantane; Saturated vapour pressure; Sublimation enthalpy; DFT calculations; Enthalpy of formation; Thermodynamic properties

1. Introduction

In the last few decades adamantane derivatives have found widespread applications in medicine due to their diverse pharmacological action. Such behaviour is likely to be determined by their specific molecular structure. The derivatives contain the hydrophobic adamantane cage (which provides penetration of these molecules straight into a cell through the lipid membrane) with various hydrophilic substituents (which are responsible for biological activity as well as relatively rapid assimilation and transportation of the substances to the required center). The spectrum of the biological activity of these medications is very wide [1–4]: they possess neuroprotective and neuromodulating action, they are also used for treatment for numerous virus diseases (e.g. influenza, hepatitis, etc.), for stimulation of the immune system, and so on. For example, amantadine and the structurally similar derivatives of 1-aminoadamantane are able to prevent disfunction and death of nerve cells under a number of different

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cerebral afflictions such as Parkinson's and Alzheimer's diseases, hypoxic brain damage, neuroinfections and stroke [1]. It should be pointed out that the syntheses of the pharmaceutically active adamantane derivatives are characterized by low yields of the target products (less than 10%). The optimization of the conditions of their production requires detailed thermodynamic information.

1-Bromoadamantane is an intermediate in the synthesis of the majority of the adamantane-based drugs. The investigation of the thermodynamic properties of 1-bromoadamantane in the condensed state was presented earlier [5]. The study of its properties in the gaseous state is also important since this information can be used to offer an optimal way to organize the purification process both for intermediates and target products at different production stages. Furthermore, this can enable technologists to take into account a possible loss of the substance because of its volatility. That is why the experimental and theoretical investigation of the thermodynamic properties for 1-bromoadamantane in the gaseous state has been carried out in the present work.

2. Experimental

2.1. Sample preparation

A commercial sample of 1-bromoadamantane (Aldrich Chem. Co., Inc.) with the mass fraction purity >0.99 was purified by triple recrystallization from acetone and subsequent sublimation at $T = 313$ K and $p = 0.4$ kPa. The final mass fraction purity of the sample obtained was 0.9984 as determined by g.l.c. with a flame-ionization detector. A single peak associated with the impurity was detected in the descending branch of the main peak. The impurity is likely to be 2-bromoadamantane—a structural isomer of 1-bromoadamantane. In this case, it would give a minor contribution to the vapour pressure and the sublimation enthalpy of the target compound.

2.2. The calorimetric determination of the sublimation enthalpy

The measurement of the sublimation enthalpy for 1-bromoadamantane was performed in a differential heat-conducting microcalorimeter of the Calvet type MID-200 with special calorimetric cells described earlier [6,7]. In every individual experiment, a sample was placed into one of the stainless-steel cells that was then hermetically sealed with a nickel membrane. The calorimeter was equilibrated to a constant temperature and afterwards the membrane was punctured with a special removable needle. The substance was sublimed in vacuum with residual pressure of about 1–0.1 Pa. The electric signal proportional to the heat flow induced by the evaporation process was recorded by a voltmeter. The uncertainty of the sublimation enthalpy determination was found to be: $\pm 5 \times 10^{-3} \times \Delta_{\mathrm{sub}} H^{\circ}_{\mathrm{m}}$ [6,7].

The molar enthalpy of sublimation $\Delta_{\mathrm{sub}} H^{\circ}_{\mathrm{m}}$ for the compound under study was calculated with the following equation:

$$\Delta_{\mathrm{sub}} H^{\circ}_{\mathrm{m}} = (Km)^{-1} \cdot M \cdot \int_{t=0}^{\tau} \Delta E \, \mathrm{d}t, \tag{1}$$

where m is the mass of the sample under vacuum; M its molar mass; K the calorimetric constant of the cell at the average temperature; ΔE the thermocouple voltage corresponding to the temperature difference between the cell and the thermostat at the point in time t; $\int_{t=0}^{\tau} \Delta E \, \mathrm{d}t$ the integrated signal recorded by the voltmeter in the course of the experiment; τ is the duration of the experiment.

The calibration of the cells used in the present work was carried out in a series of independent experiments using chromatographic-purity naphthalene since there are reliable data on the thermodynamics of its sublimation [8,9]: $\Delta_{\mathrm{sub}} H^{\circ}_{\mathrm{m}}$ (298.15 K) = 72.60 ± 0.60 kJ mol^{-1} and $\Delta^{\mathrm{g}}_{\mathrm{cr}} C^{\circ}_{\mathrm{p}} = -(34 \pm 2)$ J K^{-1} mol^{-1}.

2.3. The integral Knudsen effusion method

The saturated vapour pressures over two crystalline phases of 1-bromoadamantane in the temperature range 288–323 K were determined by the integral Knudsen effusion method. The device construction and the measurement procedure were described in detail earlier [10]. The uncertainty of the vapour pressure determination by the Knudsen method did not exceed $\pm 5 \times 10^{-2} \times p_{\mathrm{sat}}$.

In most cases, solid organic compounds have small values of thermal conductivity and, hence, an increase in the contact surface of the solid substances with the walls of an effusion chamber is of great importance for facilitating heat transfer. The evaporation surface should also be enlarged in order to accelerate attainment of equilibrium in the system 'condensed phase—vapour', especially under conditions of dynamic effusion. Both these ideas have been realized in a new modified effusion cell (Fig. 1) for the determination of vapour pressures of solid substances. The cylindrical container of 27 mm length and 10 mm internal diameter was made of stainless steel. Sixteen canals (1 mm diameter and 17 mm length) were drilled in the base of the cell. Before the measurements, a thin layer of the substance was spread all over the inner walls of the cell and then pressed against them.

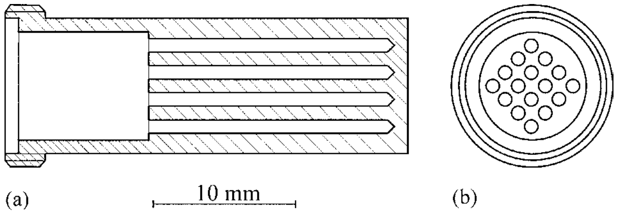


Fig. 1. The scheme of the modified cell for the effusion measurements of saturated vapour pressures of solid samples: (a) the sectional view and (b) the view from above.

Thus, the sublimation surface (this term is used by analogy with the term “evaporation surface”) was nearly equal to the inner surface area of the cell. Capillary effects were found to have a negligible influence on the vapour pressure. The cell construction and the loading procedure made it possible to get a 10-fold increase in the sublimation surface in comparison with a simple chamber-type cell, which is usually used for liquid samples. In the present work, the accuracy of the measurements with the use of the modified effusion cell was verified in experiments with benzoic acid ($K-1$ grade, mass fraction ≥ 0.99995) [8]. These results were compared with those obtained with the simple chamber-type cell (see Section 3.1).

Nickel membranes with the following parameters were used for the effusion measurements: one of thickness $l = 50 \pm 1$ μm with the average diameter of the effusion orifice of $d = 0.1833 \pm 0.0004$ mm and one of 84 ± 1 μm thickness with its orifice diameter of 0.4467 ± 0.0005 mm.

The calculation of the vapour pressure p_{sat} followed the expression:

$$p_{\mathrm{sat}} = \frac{\Delta m}{kS\tau} \cdot \left(\frac{2\pi RT}{M}\right)^{1/2}, \tag{2}$$

where Δm is the mass loss of the sample during the exposition time τ in vacuum; S the cross-sectional area of the effusion orifice; T the average temperature in the experiment; M the molar mass of the substance; $R = 8.31447\ \mathrm{J\,K^{-1}\,mol^{-1}}$; k is the probability of the transmission of the molecules through the orifice. In all the experiments, the vapours in the cell were assumed to have monomolecular composition and to be close to their saturation value due to the ratio of the sublimation surface to the orifice cross-section.

The difference between the mean free paths (λ) for a molecule deeply inside the cell and near the effusion orifice has to be taken into account as was shown earlier [10] with cyclohexyl esters. Such a violation of gas isotropy is not considered in the calculations of the transmission probability (k) according to relations commonly accepted at present. For example, with the use of the Kennard distribution [11]:

$$k = \left(1 + \frac{l}{d}\right)^{-1} \tag{3}$$

where l is the membrane thickness and d is the diameter of the effusion orifice, the calculated values of the vapour pressure appear to be 20–30% overstated, especially when the Knudsen number ($Kn = \lambda/d$) is less than 10. In the present work, the calculation of the saturated vapour pressure has been carried out according to the Wahlbeck theory [10,12], which takes into consideration the fact that the gas isotropy fails close to the effusion orifice. In terms of this theory, the transmission probability ($k = k_{\mathrm{W}}$) depends on the membrane parameters l and d as well as the mean free path of molecules (λ), the latter one being found from the expression:

$$\lambda = \frac{k_{\mathrm{B}}T}{\pi\sigma^2 p_{\mathrm{sat}}\sqrt{2}}, \tag{4}$$

where k_{B} is the Boltzmann constant and σ is the effective diameter of the molecule (the so called collision diameter) [10]. The effective diameter for the molecules of benzoic acid ($\sigma = 0.611$ nm) and 1-bromoadamantane ($\sigma = 0.716$ nm) were obtained from their geometries (with regard to the van der Waals volumes inaccessible to the same molecules) calculated with the molecular mechanics method using the MM3 force field [13] in the Tinker 4.0 package [14].

3. Results

3.1. *A test of the technique for measuring vapour pressures*

The saturated vapour pressures measured over crystalline benzoic acid by the Knudsen effusion method with the use of the modified effusion cell (Fig. 1) as well as the simple chamber-type cell are presented in Table 1. The values of the vapour pressure determined using the simpler cell are systematically lower (by about 15%) than those obtained with the modified cell. This is evidence of the fact that in the second case the temperature of the sample is closer to that set by the thermostat due to the enlargement of the contact surface of the substance with the cell walls. The deviation of the p_{sat} values obtained with the improved cell from those recommended in the TRC tables [8] do not exceed 5% whereas for the simple chamber-type cell it is as much as 20%. This is why the modified cell was used for the measurements of the saturated vapour pressure for 1-bromoadamantane.

Table 1
The saturated vapour pressure (p_{sat}) of crystalline benzoic acid ($M = 122.036\ \mathrm{g\,mol^{-1}}$, $\sigma = 0.611$ nm, $R = 8.31447\ \mathrm{J\,K^{-1}\,mol^{-1}}$)[a]

T (K)	τ (s)	Δm (mg)	k_{W}	Kn	p_{sat} (Pa)	p_{sat} (ref.) (Pa)[b]
The cell with simple cylindrical chamber						
322.99	18000	10.06	0.8930	4.1	1.485	1.807
327.85	10800	10.06	0.9169	2.5	2.429	2.972
332.75	7200	11.20	0.9481	1.6	3.951	4.834
The modified cell with enlarged sublimation surface						
318.02	25200	9.62	0.8795	5.8	1.022	1.069
322.70	3600	2.31	0.8988	3.6	1.693	1.754
322.99	18000	11.91	0.9002	3.5	1.744	1.807
327.90	14520	16.28	0.9275	2.1	2.890	2.987
332.60	7200	13.10	0.9592	1.4	4.567	4.764

[a] The membrane of 84 ± 1 μm thickness with the diameter of the effusion orifice of 0.4467 ± 0.0005 mm; Δm is the experimental mass loss of the sample during time τ at temperature T; k_{W} the transmission probability according to Wahlbeck [10,12]; p_{sat} the saturated vapour pressure obtained in this work; Kn is the Knudsen number.

[b] p_{sat} (ref.) are the values of the saturated vapour pressure recommended in the TRC tables [8].

Table 2
The saturated vapour pressure (p_{sat}) over two crystalline phases of 1-bromoadamantane ($M = 215.136\,\mathrm{g\,mol^{-1}}$, $\sigma = 0.716\,\mathrm{nm}$, $R = 8.31447\,\mathrm{J\,K^{-1}\,mol^{-1}}$)[a]

T (K)	τ (s)	Δm (mg)	k_W	Kn	p_{sat} (Pa)
Crystal II[b]					
288.36	10800	9.42	0.9186	2.4	1.603
293.31	7200	10.82	0.9524	1.5	2.687
298.28	5400	13.31	0.9893	0.95	4.279
303.22	3600	14.78	1.031	0.60	6.896
308.19	3602	24.51	1.071	0.38	11.10
Crystal I[c]					
313.16	3600	5.55	0.9535	0.61	16.90
314.21	7227	11.67	0.9569	0.59	17.66
314.65	7200	12.19	0.9603	0.56	18.47
315.63	5400	9.69	0.9645	0.54	19.52
316.65	5400	10.74	0.9719	0.49	21.50
318.12	5400	12.12	0.9804	0.44	24.11
320.59	3600	9.90	0.9941	0.36	29.25
323.03	3600	11.84	1.005	0.31	34.72

[a] The notations are identical to those in Table 1.

[b] The membrane of thickness $l = 84 \pm 1\,\mu\mathrm{m}$ with the diameter of the effusion orifice of $d = 0.4467 \pm 0.0005$ mm was used.

[c] The membrane of $50 \pm 1\,\mu\mathrm{m}$ thickness with the average orifice diameter of 0.1833 ± 0.0004 mm was used.

3.2. The saturated vapour pressure and the enthalpy of sublimation for 1-bromoadamantane

The results of the vapour pressure determination for two crystalline phases of 1-bromoadamantane between $T = 288$ and 323 K are summarized in Table 2 and shown in Fig. 2. The measurements were carried out in such a manner that the p_{sat} values for these individual phases (crII and crI) were obtained with the membranes having diverse orifice diameters.

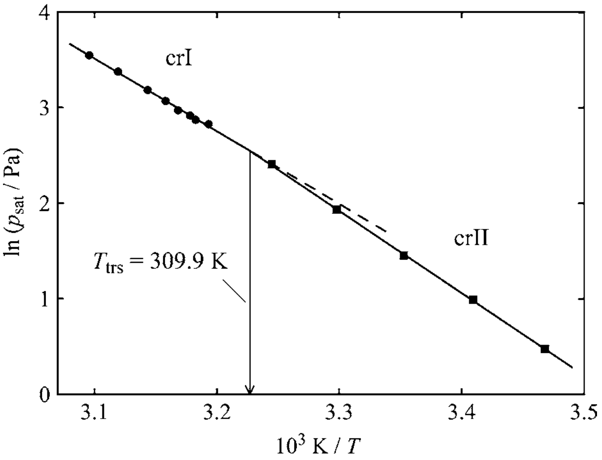


Fig. 2. The temperature dependence of the saturated vapour pressure for 1-bromoadamantane between $T = 288$ and 323 K (crI and crII): black rectangles are the results obtained with the use of the membrane of $84 \pm 1\,\mu\mathrm{m}$ thickness and the orifice diameter of 0.4467 ± 0.0005 mm; black circles are the results of the measurements with the membrane of $50 \pm 1\,\mu\mathrm{m}$ thickness and the diameter of the effusion orifices of 0.1833 ± 0.0004 mm; dotted line is the temperature dependence of the vapour pressure for crI extrapolated into the region where crII is the equilibrium phase, for purposes of visualization.

Table 3
The comparison of the results from the independent determinations of the sublimation enthalpy and the standard entropy for 1-bromoadamantane

Property	Method[a]	crII ($T = 303.0$ K)	crI ($T = 317.0$ K)
$\Delta_{sub}H_m^\circ(T)$ (kJ mol^{-1})	eff	71.3 ± 1.1[b]	63.2 ± 2.1
	cal	71.77 ± 0.31	
	av	71.74 ± 0.30	
p_{sat} (Pa)	eff	6.79 ± 0.09	22.1 ± 0.2
$\Delta_0^T S_m^\circ$(cr) (J K^{-1} mol^{-1})	cal	220.3 ± 1.1 [5]	254.8 ± 1.2 [5]
$\Delta_0^T S_m^\circ$(g) (J K^{-1} mol^{-1})	exp	377.2 ± 1.5	384.2 ± 6.7
	calc	376.4 ± 1.9	384.3 ± 1.9

[a] The abbreviations: eff is the Knudsen effusion method; cal is the calorimetric method; av the average weighted value; exp and calc are the values of the standard entropy determined experimentally (Section 3.2) and calculated by the statistical thermodynamics (Section 4.1), respectively.

[b] The value adjusted to $T = 303.0$ K with $\overline{\Delta_{crII}^{g}C_p^\circ} = -(47.4 \pm 1.2)\,\mathrm{J\,K^{-1}\,mol^{-1}}$ for the temperature range 298.1–303.3 K. The value of the enthalpy of sublimation at the average temperature of the series of the effusion measurements is $\Delta_{sub}H_m^\circ(298.1\,\mathrm{K}) = 71.6 \pm 1.1\,\mathrm{kJ\,mol^{-1}}$.

The temperature of the crII → crI transition for the compound under study ($T_{trs} = 309.9$ K) has been previously determined by adiabatic calorimetry with high accuracy [5]. In this connection, the experimental values of p_{sat} of these two phases were fitted by the method of least-squares using the condition p_{sat} (crII) = p_{sat} (crI) at $T = T_{trs}$. Thus, the temperature dependences of p_{sat} for crII in the temperature range 288.4–309.9 K and for crI between $T = 309.9$ and 323.0 K are well described by the following equations:

$$\ln\{p_{sat}(\mathrm{crII})\,(\mathrm{Pa})\} = (30.33 \pm 0.44) - (8608 \pm 137) \cdot (T(\mathrm{K}))^{-1}, \tag{5}$$

$$\ln\{p_{sat}(\mathrm{crI})\,(\mathrm{Pa})\} = (27.07 \pm 0.81) - (7600 \pm 252) \cdot (T(\mathrm{K}))^{-1}. \tag{6}$$

The sublimation enthalpies (Table 3) for 1-bromoadamantane at the average temperatures of the series obtained were derived from Eqs. (5) and (6). The enthalpy of the solid-to-solid phase transition crII → crI was also estimated with the use of Eqs. (5) and (6) by difference: $\Delta_{trs}H_m^\circ \approx 7.3 \pm 2.4\,\mathrm{kJ\,mol^{-1}}$. For this purpose, the $\Delta_{sub}H_m^\circ$ values for both phases were first adjusted to the transition temperature of $T_{trs} = 309.9$ K using the values of $\overline{\Delta_{crII}^{g}C_p^\circ} = -(46.9 \pm 1.2)\,\mathrm{J\,K^{-1}\,mol^{-1}}$ for the temperature range 298.1–309.9 K and $\overline{\Delta_{crI}^{g}C_p^\circ} = -(71.6 \pm 1.3)\,\mathrm{J\,K^{-1}\,mol^{-1}}$ for the range from 309.9 to 317.0 K: the heat capacities of crystals and gas are presented in [5] and in Section 4.1 of the present work, respectively. The value of the phase-transition enthalpy obtained thus is in good agreement with the values measured by adiabatic calorimetry, $\Delta_{trs}H_m^\circ = 7.42 \pm 0.01\,\mathrm{kJ\,mol^{-1}}$ [5], and by DSC, $\Delta_{trs}H_m^\circ = 7.51 \pm 0.15\,\mathrm{kJ\,mol^{-1}}$ [5].

The enthalpy of sublimation for crII of 1-bromoadamantane was also determined by averaging the results of

Table 4
The results of the calorimetric measurements of the molar sublimation enthalpy ($\Delta_{\rm sub}H^\circ_{\rm m}$) for 1-bromoadamantane ($M = 215.136\ {\rm g\,mol^{-1}}$)[a]

T (K)	m (mg)	$\int_{t=0}^{\tau}\Delta E\,{\rm d}t$ (mV s)	Type of cell[b]	$\Delta_{\rm sub}H^\circ_{\rm m}$ (kJ mol^{-1})
303.52	50.59	3178.98	A	72.52
302.57	70.96	4376.98	A	71.18
302.70	54.60	3380.12	A	71.45
302.62	68.50	4240.78	A	71.45
303.20	50.51	3144.98	A	71.86
303.71	62.54	3970.74	B	72.32
302.62	64.08	4019.41	B	71.44
302.74	61.79	3890.81	B	71.71
302.64	59.94	3768.66	B	71.61
303.19	45.94	2909.20	B	72.13

$\langle\Delta_{\rm sub}H^\circ_{\rm m}({\rm crII}, 303.0\ {\rm K})\rangle = 71.77 \pm 0.31$[c]

[a] m is the mass of the sample (adjusted to the vacuum conditions); $\int_{t=0}^{\tau}\Delta E\,{\rm d}t$ the integrated electric signal recorded by the voltmeter in the course of the experiment; T the temperature of the experiment; τ is the duration of the experiment.

[b] $K_{\rm A} = 186.4 \pm 0.5\ {\rm mV\,s\,J^{-1}}$ and $K_{\rm B} = 188.9 \pm 0.9\ {\rm mV\,s\,J^{-1}}$.

[c] The average value.

the series of 10 independent calorimetric experiments carried out in the differential heat-conducting calorimeter MID-200 (Table 4). As it can be seen from Table 3, the data of the calorimetric and effusion measurements of the sublimation enthalpy agree well within the experimental errors. An average weighted value of $\Delta_{\rm sub}H^\circ_{\rm m}$ (Table 3) was calculated from these values. The experimental standard entropy of gaseous 1-bromoadamantane at two temperatures (Table 3) was calculated from the data on the thermodynamics of sublimation determined in this work and the values of the standard entropy for crII and crI obtained previously [5].

4. Calculations

4.1. The thermodynamic properties of 1-bromoadamantane in the ideal gaseous state

The computational procedure for the calculation of the thermodynamic properties of organic substances in the ideal gaseous state by the statistical thermodynamic method was described in detail in [15]. The absence of tops in the molecule of 1-bromoadamantane and the rigidity of the adamantane cage structure (Fig. 3) made the computations simpler. The molar mass of 1-bromoadamantane is $M = 215.136\ {\rm g\,mol^{-1}}$ and its symmetry number is $n = 3$. The other necessary molecular (the principal moments of inertia) and spectral (the frequencies of its normal vibrations) characteristics have been obtained in the present work.

The Raman spectrum (Fig. 4) for crystalline 1-bromoadamantane in the range from 100 to 3500 cm^{-1} at ambient temperature was recorded on a LabRam Raman microscope (HORIBA Jobin Yvon, Inc.) supplied with a CCD detection system and an Olympus confocal microscope.

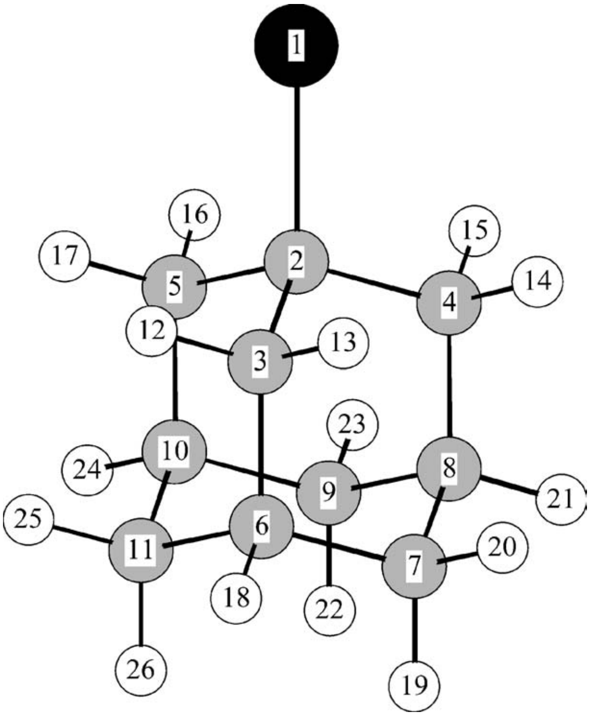


Fig. 3. The structural formula of 1-bromoadamantane: a black circle is bromine atom; grey circles are carbon atoms; white circles are hydrogen atoms.

The 632.8 nm line of the helium–neon laser was used for excitation. The experimental values of the fundamentals for the compound under study are listed in Table 5. In addition to the Raman spectroscopic data, the IR spectrum of 1-bromoadamantane was taken from [16,17].

The molecule of 1-bromoadamantane belongs to C_{3v} point group. In terms of the group-theoretical analysis, its 72 normal vibrational modes can be distributed among the following irreducible representations: $\Gamma = 16A_1 + 8A_2 + 24E$. The normal modes with the A_2 symmetry are both IR and Raman inactive. That is why quantum-mechanical calculations were

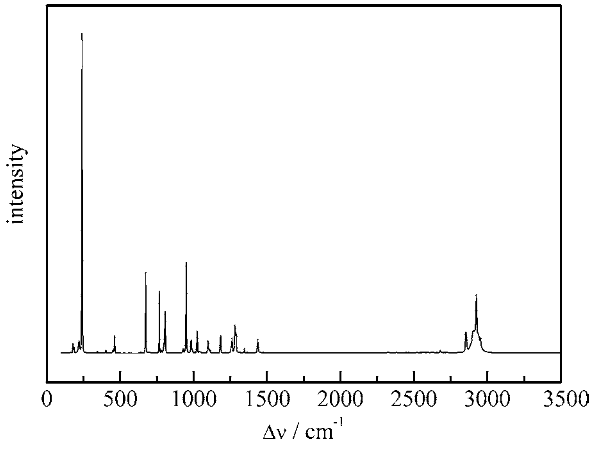


Fig. 4. The Raman spectrum of crystalline 1-bromoadamantane.

Table 5
The experimental and calculated (B3LYP/6-31G*) fundamentals (in cm^{-1}) for 1-bromoadamantane

Symmetry	$\tilde{\nu}_{exp}$[a]			$\tilde{\nu}_{calc}$		$\tilde{\nu}$[b]
	IR [16]	IR [17]	Raman [this work]	Non-scaled[c]	Scaled[d]	
E	2940 vs	2935 s	2954 m	3096 (63)	2950	2945
A_2				3091 (−)	2945	2945
A_1		2925 vs	2925 vs	3070 (136)	2925	2925
E				3064 (31)	2919	2925
A_1				3063 (15)	2919	2925
E	2915 vs	2910 vs		3055 (136)	2911	2910
A_1			2905 m	3048 (83)	2904	2905
E				3044 (37)	2900	2905
A_1	2860 vs	2855 v	2854 m	3027 (20)	2884	2855
E				3027 (27)	2884	2855
A_1		1474 w	1475 vw	1546 (0.2)	1476	1475
A_1	1453 s	1456 vs	1457 vw	1525 (13)	1457	1455
E	1450 sh	1450 sh		1520 (13)	1453	1450
E			1436 m	1508 (0.1)	1442	1436
E	1366 vw	1366 w	1364 vw	1413 (0.2)	1359	1365
A_1	1347 m	1343 m	1345 w	1399 (1.2)	1347	1345
E	1344 m			1392 (<0.1)	1340	1344
A_2			1318 vw	1364 (−)	1315	1318
E	1312 vw	1311 vw	1311 vw	1358 (1.5)	1310	1311
A_1	1292 vs	1291 s	1288 sh	1333 (47)	1288	1290
E	1286 sh		1281 s	1321 (0.1)	1277	1281
A_2				1321 (−)	1277	1281
E	1256 vw	1262 w	1263 m	1301 (<0.1)	1258	1260
E	1181 vw	1184 w	1184 m	1214 (0.3)	1179	1184
A_2				1141 (−)	1112	1113
A_2			1113 vw	1136 (−)	1107	1113
E	1103 m	1099 m	1098 m	1130 (5.2)	1101	1100
A_1				1126 (0.5)	1098	1100
E	1057 vw	1049 w	1047 vw	1056 (<0.1)	1033	1048
A_2		1038 vw	1039 vw	1056 (−)	1033	1039
A_1	1030 vs	1026 vs	1024 m	1049 (66)	1026	1025
E	987 w	985 w	984 m	996 (1.9)	977	985
A_1	950 m	950 m	950 s	966 (19)	948	950
E		934 vw	928 w	938 (0.2)	922	928
A_2				913 (−)	898	898
E		896 w		905 (<0.1)	890	896
A_1	813 vs	805 s	805 s	817 (61)	805	805
E	797 vw	791 vw		814 (0.6)	802	791
A_1	766 m	765 m	767 s	767 (7.6)	758	766
A_1	676 s	675 s	674 s	687 (25)	680	675
E		641 w	641 vw	651 (0.6)	645	641
A_1		463 m	462 m	463 (8.0)	461	462
E			449 vw	448 (0.1)	446	449
E			403 vw	405 (0.2)	403	403
E			343 vw	346 (<0.1)	345	343
A_2				313 (−)	312	312
A_1			241 vs	247 (12)	246	241
E			179 m	181 (0.6)	181	179

[a] The abbreviations for the intensity of spectral bands: vs, s, m, w and vw are very strong, strong, medium, weak, and very weak, respectively; sh is a ‘shoulder’ on a distinct band. The IR spectra were recorded for the solution of 1-bromoadamantane in CCl_4 only down to 650 cm^{-1} [16] and for the crystalline sample down to 400 cm^{-1} [17].

[b] The fundamentals chosen for calculations by the statistical thermodynamics.

[c] The IR intensities in (10^{14} C^2 kg^{-1}) are given in parentheses, the dash denoting prohibition of a vibration with certain symmetry in the IR spectrum.

[d] The scaling factors were obtained in the present work (Eqs. (7) and (8)).

necessary in obtaining the complete set of the fundamentals and determining the symmetry of the vibrations corresponding to certain experimental bands.

The geometry optimization for 1-bromoadamantane, the computation of the frequencies of its normal modes and their intensities in the IR spectrum were performed in terms of the density functional theory (B3LYP functional [18,19]) in the standard 6-31G* basis set with the use of the PC GAMESS package (version 6.4) [20]. According to the quantum calculations, the total energy of 1-bromoadamantane

Table 6
The calculated and experimental bond lengths and valence angles for the isolated molecule of 1-bromoadamantane[a]

Parameter[b]	B3LYP/6-31G*	Experiment [21][c]
$Br_{(1)}—C_{(2)}$	0.2007	0.1947 ± 0.0006
$C_{(2)}—C_{(3)}$	0.1534	0.1542 ± 0.0003
$C_{(3)}—C_{(6)}$	0.1548	0.1542 ± 0.0003
$C_{(6)}—C_{(7)}$	0.1543	0.1542 ± 0.0003
$C_{(3)}—H_{(12)}$	0.1096	0.109
$C_{(6)}—H_{(18)}$	0.1098	0.109
$C_{(7)}—H_{(19)}$	0.1098	0.109
$C_{(7)}—H_{(20)}$	0.1099	0.109
$Br_{(1)}—C_{(2)}—C_{(3)}$	108.5	109.5
$C_{(3)}—C_{(2)}—C_{(4)}$	110.4	109.5
$C_{(2)}—C_{(3)}—C_{(6)}$	108.5	109.5
$C_{(3)}—C_{(6)}—C_{(7)}$	109.4	109.5
$C_{(6)}—C_{(7)}—C_{(8)}$	109.6	109.5
$C_{(7)}—C_{(8)}—C_{(9)}$	109.6	109.5
$C_{(2)}—C_{(3)}—H_{(12)}$	110.0	109.5
$C_{(3)}—C_{(6)}—H_{(18)}$	108.8	109.5
$C_{(6)}—C_{(7)}—H_{(19)}$	110.0	109.5
$C_{(6)}—C_{(7)}—H_{(20)}$	110.1	109.5
$C_{(7)}—C_{(6)}—H_{(18)}$	109.9	109.5
$C_{(6)}—C_{(3)}—H_{(12)}$	110.5	109.5
$H_{(12)}—C_{(3)}—H_{(13)}$	107.3	109.5
$H_{(19)}—C_{(7)}—H_{(20)}$	106.9	109.5

[a] The bond lengths are presented in nm, the valence angles are in degrees.

[b] There are nine groups of atoms discernible according to their nature and their nearest neighbours (Fig. 3, subscript is an atom number): I—$Br_{(1)}$; II—$C_{(2)}$; III—$C_{(3)}$, $C_{(4)}$ and $C_{(5)}$; IV—$C_{(6)}$, $C_{(8)}$ and $C_{(10)}$; V—$C_{(7)}$, $C_{(9)}$ and $C_{(11)}$; VI—$H_{(12)}$, $H_{(13)}$, $H_{(14)}$, $H_{(15)}$, $H_{(16)}$ and $H_{(17)}$; VII—$H_{(18)}$, $H_{(21)}$ and $H_{(24)}$; VIII—$H_{(19)}$, $H_{(22)}$ and $H_{(26)}$; IX—$H_{(20)}$, $H_{(23)}$ and $H_{(25)}$.

[c] On the treatment of the microwave spectrum, it was taken in [21] that the C–H bond lengths were equal to 0.109 nm and all the valence angles were tetrahedral.

molecule made up $E_{tot} = -2961.878863$ au. The molecular geometric parameters obtained as a result of these quantum computations are summarized in Table 6. Based on these data, the product of the principal moments of inertia for 1-bromoadamantane molecule was derived to be $I_A \cdot I_B \cdot I_C = 1.183 \times 10^{-132}$ kg^3 m^6; this value was used in further calculations using statistical thermodynamics.

The geometric parameters of 1-bromoadamantane determined from the results of the microwave spectroscopic investigation [21] are also presented in Table 6. Except for the length of the C–Br bond, all the other calculated parameters appeared to be quite close to the experimental ones. However, it should be emphasized that the experimental and calculated bond lengths and valence angles cannot be directly compared. That is because quantum calculations provide an equilibrium geometry at $T = 0$ K, whereas in the case of using results from microwave spectroscopy, anharmonicity has an effect resulting in thermal averaging of geometrical parameters. Knowledge of the vibrational amplitudes at the temperature of the spectroscopic measurements is necessary for the adjustment of the experimental results to the equilibrium geometry. However, such an adjustment was not carried out for 1-bromoadamantane in [21].

The fundamentals calculated with B3LYP/6-31G* for 1-bromoadamantane are listed in Table 5. The correspondence between the experimental and calculated values of the frequencies of the normal modes was set up according to the experimental intensities of the IR bands and those calculated quantum-mechanically. The masses of the most abundant isotopes of bromine (bromine-79 and -81) differ from each other by only a few percent. That is why it was impossible to experimentally separate the frequencies of the normal modes involving the individual isotopes of bromine. In this connection, the computation of the fundamentals for 1-bromoadamantane was performed only for the molecule containing bromine-79.

Vibrational frequencies calculated quantum-mechanically are usually higher than the experimental ones due to an approximate consideration of the dissociative behaviour of bonds and of electron correlation as well as the neglect of the anharmonicity effects. That is why the calculated values of fundamentals should be multiplied by certain scaling factors. The use of the scaling factors from [22] has resulted in the systematic overstatement of the calculated fundamentals in relation to the experimental frequencies for the compound under study.

The numerical values of the scaling factors for B3LYP/6-31G* were evaluated in the present work. The dependence of the scaling factor (χ) on the wave-number ($\tilde{\upsilon}$) in the range from 100 to 1500 cm^{-1} was determined to be:

$$\chi = (0.9983 \pm 0.0042) - (1.83 \pm 0.23) \times 10^{-8} \times (\tilde{\upsilon})^2. \tag{7}$$

The single value:

$$\chi = 0.9528 \pm 0.0019 \tag{8}$$

was calculated separately for the wave-number region from 2800 to 3000 cm^{-1} associated with the C–H stretching vibrations. Eqs. (7) and (8) were obtained by least-squares fitting according to the procedure described in [22]: the fundamentals calculated using B3LYP/6-31G* for all the participants of the homodesmic reaction described in Section 4.2 were used (Table 5 and Table S.1 of Supplementary Data). The required experimental values of the fundamentals were taken from [23] for adamantane, from [17,24] for 2-bromo-2-methylpropane, and from [25] for 2-methylpropane. Since the set of molecules used for obtaining Eqs. (7) and (8) is rather scanty these equations should not be spread on other organic compounds.

The average and maximum deviations between calculated (scaled) and experimental fundamentals for 1-bromoadamantane amount to 4 and 15 cm^{-1}, respectively. The hardly analyzable region from 2800 to 3000 cm^{-1} corresponding to the C–H stretching vibrations was not included into this analysis because these frequencies give a negligible effect on the thermodynamic functions.

In addition to the B3LYP/6-31G* computation, similar quantum calculations of the frequencies of the normal modes of 1-bromoadamantane were performed with the use of the B3LYP/6-311G** and RHF/6-31G* basis sets (Table S.2 of Supplementary Data). In the first case, extension of the basis set leads to an increase in computation time nearly by a factor of three but does not give rise to better agreement between the calculated and experimental wavenumbers (for B3LYP/6-311G** the average and maximum deviations are 4 and 16 cm^{-1}). In the Hartree–Fock method there is a considerable decrease in computation time but, on the other hand, the calculated frequencies are in poorer agreement with the experimental values (for RHF/6-31G* the average and maximum deviations are 5 and 23 cm^{-1}, respectively). Thus, in the present work the B3LYP/6-31G* basis set was chosen.

The complete set of the fundamentals (Table 5) composed of the data from the IR and Raman spectroscopic study and of the results of the DFT calculations (B3LYP/6-31G*) was used for the statistical thermodynamic calculations. The experimental values of the frequencies were favoured in this process. The fundamentals obtained were verified in the calculations of the heat capacity of crystalline 1-bromoadamantane, which was described earlier in [5]. In this case, the isobaric heat capacity was presented as a sum of the lattice contribution (with the Debye temperatures Θ_{D} (3) = 72.1 K and the Einstein temperatures $\Theta_{\mathrm{E},1}$ (1) = 74.9 K, $\Theta_{\mathrm{E},2}$ (2) = 122.2 K), the contribution of the intramolecular vibrations (with the fundamentals summarized in Table 5), and the anharmonicity term with the coefficient $A = 1.28 \times 10^{-5}\ \mathrm{J}^{-1}\,\mathrm{mol}$. The numbers in parentheses are the degeneracies of the corresponding contributions. The difference between the experimental and calculated values of the isobaric heat capacity $C_{\mathrm{p,m}}$ of the compound did not exceed $\pm 4 \times 10^{-3} \times C_{\mathrm{p,m}}$ in the range 50–140 K, $\pm 7 \times 10^{-3} \times C_{\mathrm{p,m}}$ between $T = 20$ and 50 K (Fig. 5). The contribution of the intramolecular vibrations to $C_{\mathrm{p,m}}$ comprised less than $10^{-3} \times C_{\mathrm{p,m}}$ at lower temperatures.

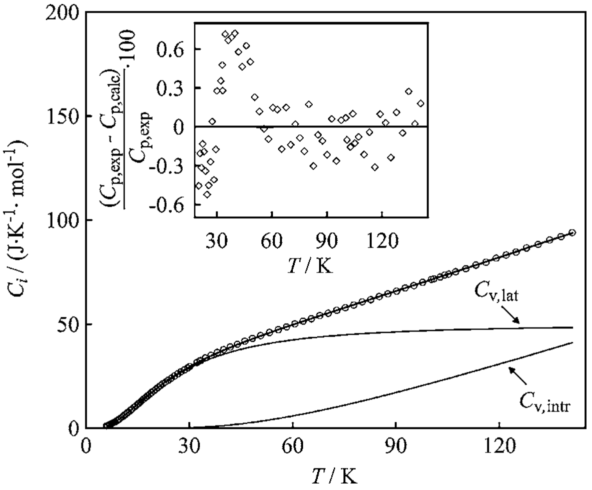


Fig. 5. The temperature dependence of different contributions to the molar isobaric heat capacity of crystalline 1-bromoadamantane: circles are the experimental heat-capacity values $C_{\mathrm{p,exp}}$; $C_{\mathrm{p,calc}}$ the isobaric heat capacities calculated according to the contributions; $C_{\mathrm{v,lat}}$ the lattice contribution to the heat capacity; $C_{\mathrm{v,intr}}$ the contribution of the intramolecular vibrations; rectangles are the percentage deviations of $C_{\mathrm{p,calc}}$ from $C_{\mathrm{p,exp}}$.

The thermodynamic properties of 1-bromoadamantane in the ideal gaseous state in the temperature range 100–1000 K are presented in Table 7. As it may be seen from Table 3, the values of the standard entropy for gaseous 1-bromoadamantane calculated by the statistical thermodynamics and determined experimentally agree well with each other within the error.

4.2. *The enthalpy of formation of 1-bromoadamantane*

The following methods were used for the calculations of the enthalpy of formation for the compound under study in the gaseous state:

(I) The formation enthalpy of 1-bromoadamantane has been obtained according to the Pedley scheme [26], in which the values of the standard enthalpy of formation for gaseous organic substances $\Delta_{\mathrm{f}} H^{\circ}_{\mathrm{m}}$(g, 298.15 K) are cal-

Table 7
The standard molar thermodynamic functions of 1-bromoadamantane in the ideal gaseous state ($R = 8.31447\ \mathrm{J\,K^{-1}\,mol^{-1}}$, $p = 10^5$ Pa)

T (K)	$C^{\circ}_{\mathrm{p,m}}/R$	$\Delta_0^{\mathrm{T}} H^{\circ}_{\mathrm{m}}/RT$	$\Delta_0^{\mathrm{T}} S^{\circ}_{\mathrm{m}}/R$	$\Phi^{\circ}_{\mathrm{m}}/R$	$\Delta_{\mathrm{f}} H^{\circ}_{\mathrm{m}}$ (kJ mol^{-1})	$\Delta_{\mathrm{f}} G^{\circ}_{\mathrm{m}}$ (kJ mol^{-1})
100	6.595	4.725	32.15	27.43	−92.47	−40.04
150	9.477	5.821	35.36	29.54	−101.6	−11.79
200	12.69	7.127	38.52	31.39	−110.5	19.46
298.15	20.18	10.16	44.94	34.78	−133.0[a]	87.62
300	20.33	10.22	45.06	34.85	−133.3	88.99
400	28.33	13.76	52.02	38.26	−162.5	168.4
500	35.34	17.39	59.12	41.72	−173.0	252.4
600	41.13	20.88	66.09	45.21	−180.5	338.3
700	45.88	24.13	72.80	48.67	−185.7	425.2
800	49.80	27.10	79.19	52.09	−188.9	512.7
900	53.09	29.81	85.25	55.44	−190.6	600.5
1000	55.87	32.28	90.99	58.71	−191.0	688.5

[a] The value obtained by the Pedley procedure (Section 4.2).

Table 8
The contributions (in kJ mol^{-1}) for the calculation of the enthalpy of formation for gaseous 1-bromoadamantane by the Pedley procedure [26]

A_a		F_i		B_{ij}		R_{cycl}[a]
Type	Value	Type	Value	Type	Value	
C	716.68	$>CH_2$	815.0	$(C{-}C)_{\text{ring}}$	358.45	23.2
H	217.998	$>CH-$	405.3	$C_{\text{tert}}{-}Br$	297.5	
Br	111.87	$>C<$	0.0			
		Br	0.0			

[a] The increment of the tricyclic cage structure of adamantane.

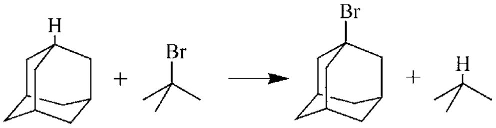
culated by the following equation:

$$\Delta_f H_m^\circ(\text{g, 298.15 K}) = \sum_a A_a - \sum_i F_i - \sum_{ij} B_{ij} + \sum_{ijk} C_{ijk} + R_{\text{cycl}}, \qquad (9)$$

where A_a are the standard enthalpies of formation of the atoms forming the compound; F_i the contributions of the individual fragments constituting the molecule of the substance; B_{ij} the increments of the individual bonds in the molecule; C_{ijk} the increments of the pairs of the adjacent bonds; R_{cycl} is the contribution of the cyclic system. The summation is over all the atoms (a), fragments (i), bonds (ij) and pairs of the adjacent bonds (ijk). According to the scheme the C_{ijk} increments are equal to zero for the mentioned compound. The other values of A_a, F_i, B_{ij} and R_{cycl} (Table 8) obtained in [26] were used for 1-bromoadamantane, with the following value being derived:

$$\begin{aligned}\Delta_f H_m^\circ(\text{g, 298.15 K})_{\text{I}} &= \{10 \cdot A(\text{C}) + 15 \cdot A(\text{H}) + A(\text{Br})\} \\ &\quad + \{6 \cdot F(> \text{CH}_2) + 3 \cdot F(> \text{CH}-) + F(> \text{C} <) \\ &\quad + F(\text{Br})\} + \{12 \cdot B(\text{C–C})_{\text{ring}} + B(\text{C}_{\text{tert}}\text{–Br})\} \\ &\quad + R_{\text{cycl}} = -133.0\,\text{kJ mol}^{-1}.\end{aligned}$$

(II) A calculational procedure in common use is determination of the enthalpy of formation of a compound through an appropriate homodesmic reaction, in which the formation enthalpies for its participants (except for the target compound) are known. In this work, the formal reaction was chosen so that the initial and final substances were chemically and structurally similar:



(10)

The enthalpies of formation of adamantane, 2-bromo-2-methylpropane, and 2-methylpropane in the gaseous state at $T = 298.15$ K were taken from [26] and they are summarized in Table 9. Two approaches for the analysis of this homodesmic reaction were used in the present work:

(IIa) The substitutive procedure for calculations of the enthalpies of formation is based on the classical theory of molecular structure and assumes additivity of properties. According to this procedure, the enthalpy of a homodesmic reaction is assumed to be zero. In terms of this approach, the value of the enthalpy of formation for 1-bromoadamantane in the gaseous state was obtained to be:

$$\Delta_f H_m^\circ(\text{g, 298.15 K})_{\text{II}} = -132.8\,\text{kJ mol}^{-1}.$$

(IIb) According to the quantum-mechanical consideration, a homodesmic reaction is assumed to be accompanied by an enthalpy change. That is why the total molecular energies (E_{tot}) and the zero-point vibrational energies (ZPVE) were calculated in B3LYP/6-31G* for all the participants of the reaction (10) (adamantane, 2-bromo-2-methylpropane, 1-bromoadamantane and 2-methylpropane). The values involved are presented in Table 9. Thus, the enthalpy of the gaseous reaction at $T = 0$ K was derived, $\Delta_r H_m^\circ(\text{g}, 0\,K) = -10.6\,\text{kJ mol}^{-1}$.

In order to adjust $\Delta_r H_m^\circ$ from $T = 0$ to 298.15 K, the values of the standard enthalpy $\Delta_0^{298.15} H_m^\circ$ for adamantane, 2-bromo-2-methylpropane and 2-methylpropane (in addition to 1-bromoadamantane) were calculated using statistical thermodynamics (Table 9). For this purpose, the following parameters of the compounds mentioned above were used: the molecular geometries from the B3LYP/6-31G* calculations; the frequencies of their normal vibra-

Table 9
The data used in the calculation of the enthalpy of formation for gaseous 1-bromoadamantane

Compound	$\Delta_f H_m^\circ$ (kJ mol^{-1})	$\Delta_0^{298.15} H_m^\circ$ (kJ mol^{-1})	E_{tot} (au)	ZPVE (kJ mol^{-1})[a]
Adamantane	−134.6 [26]	21.02	–390.726022	621.0
2-Bromo-2-methylpropane	−132.4 [26]	20.66	–2729.609304	309.4
2-Methylpropane	−134.2 [26]	18.13	–158.458813	333.4
1-Bromoadamantane	−132.8[b] −141.8[c]	25.18	–2961.878863	592.6

[a] The ZPVE values were obtained from the scaled fundamentals.
[b] The value found in this work according to the substitutive procedure.
[c] The value calculated quantum-mechanically in this work.

tions obtained from the experimental and calculated fundamentals (Table S.3 of Supplementary Data) by the procedure similar to that for 1-bromoadamantane; the rotational barriers for methyl tops $V_0 = 18.5\,\mathrm{kJ\,mol^{-1}}$ for 2-bromo-2-methylpropane and $V_0 = 14.4\,\mathrm{kJ\,mol^{-1}}$ for 2-methylpropane estimated from the corresponding fundamentals.

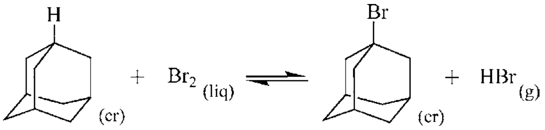
The enthalpy of the above homodesmic reaction at $T = 298.15$ K was calculated to be $\Delta_r H_m^\circ(\mathrm{g}, 298.15\,\mathrm{K}) = -9.0\,\mathrm{kJ\,mol^{-1}}$. Thus, according to the quantum-mechanical computations, the enthalpy of formation for gaseous 1-bromoadamantane is:

$$\Delta_f H_m^\circ(\mathrm{g}, 298.15\,\mathrm{K})_{\mathrm{III}} = -141.8\,\mathrm{kJ\,mol^{-1}}.$$

The $\Delta_f H_m^\circ(\mathrm{g}, 298.15\,\mathrm{K})$ values for 1-bromoadamantane from the first two approaches coincide almost completely with each other. The value calculated by the Pedley procedure was used here for the calculations of the thermodynamic properties of this substance in the gaseous state. On the base of this value, the enthalpies and the Gibbs free energies of formation for 1-bromoadamantane in the temperature range from 100 to 1000 K (Table 7) were calculated, the thermodynamic functions of elements (carbon, hydrogen and bromine) being taken from [27].

4.3. The thermodynamic analysis of some reactions involving 1-bromoadamantane

The bromination of adamantane is one of the cheapest and the most rational ways for functionalizing the adamantane molecule. Moreover, under certain conditions [28] this reaction is rather selective, with 1-bromoadamantane being predominantly formed. According to [28], 1-bromoadamantane is formed during heterogeneous bromination of adamantane in the absence of any solvent:



(11)

The thermodynamic analysis of the above reaction at $T = 298.15$ and 332.3 K has been performed in the present work. The latter temperature refers to the boiling temperature of bromine at $p = 10^5$ Pa [27]. The results of calculations of the Gibbs free energy of reaction (11) $\Delta_r G_m^\circ(T)$ and its equilibrium constant K_p° at these two temperatures are presented in Table 10. In the table, in those cases where literature sources are not indicated, the experimental or calculated values of the properties for the reaction participants were obtained in the present work. The equilibrium constant for the reaction of the homogeneous adamantane bromination in the gaseous phase at $T = 298.15$ K is also presented in Table 10 for comparison purposes. It is apparent that the equilibrium of the reaction of monobromination of adamantane with the formation of 1-bromoadamantane is offset towards the latter one almost entirely over a wide temperature range. Furthermore, this process is realized under atmospheric pressure in such a way that gaseous hydrogen bromide escapes constantly from the reaction medium. This being so, the reaction involved can be taken with certainty to be virtually irreversible.

The hydrolysis of 1-bromoadamantane is an important reaction applied in the pharmaceutical industry to form 1-hydroxyadamantane, another important intermediate in the synthesis of adamantane-based medicines. In this work, the thermodynamics of this reaction in the gaseous state has

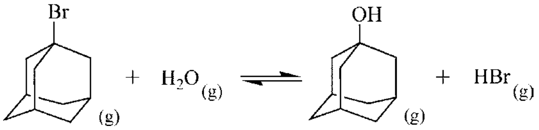
Table 10
The thermodynamic analysis of the reaction of bromination of adamantane

Property	Adamantane	Br_2	1-Bromoadamantane	HBr
$T = 298.15$ K				
Phase	Crystal I	Liquid	Crystal II	Gas
$\Delta_f H_m^\circ$ ($\mathrm{kJ\,mol^{-1}}$)	−194.1 [26]	0	−205.0	−36.29 [27]
$\Delta_0^T S_m^\circ$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	195.8 [29]	152.2 [27]	216.8 [5]	198.7 [27]
$\Delta_r G_m^\circ = -67.3\,\mathrm{kJ\,mol^{-1}}$ and $K_p^\circ = 6.2 \times 10^{11}$				
$T = 298.15$ K				
Phase	Gas	Gas	Gas	Gas
$\Delta_f H_m^\circ$ ($\mathrm{kJ\,mol^{-1}}$)	−134.6 [26]	30.91 [27]	−133.0	−36.29 [27]
$\Delta_0^T S_m^\circ$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	321.3	245.5 [27]	373.6	198.7 [27]
$\Delta_r G_m^\circ = -67.2\,\mathrm{kJ\,mol^{-1}}$ and $K_p^\circ = 6.0 \times 10^{11}$				
$T = 332.3$ K				
Phase	Crystal I	Liquid	Crystal I	Gas
$\Delta_{298.15}^{332.3} H_m^\circ$ ($\mathrm{kJ\,mol^{-1}}$)	6.91 [29]	2.58 [27]	15.85 [5]	0.996 [27]
$\Delta_0^T S_m^\circ$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	217.8 [29]	160.4 [27]	267.4 [5]	201.8 [27]
$\Delta_r G_m^\circ = -70.1\,\mathrm{kJ\,mol^{-1}}$ and $K_p^\circ = 1.0 \times 10^{11}$				

Table 11
The thermodynamic analysis of the reaction of hydrolysis of 1-bromoadamantane

Property	1-Bromoadamantane	H_2O	1-Hydroxyadamantane	HBr
$T = 298.15$ K				
Phase	Gas	Gas	Gas	Gas
$\Delta_f H_m^\circ$ ($\mathrm{kJ\,mol^{-1}}$)	−133.0	−241.8 [27]	−310.9 [8]	−36.29 [27]
$\Delta_0^T S_m^\circ$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	373.6	188.8 [27]	366.2 [8]	198.7 [27]
$\Delta_r G_m^\circ = 26.9\,\mathrm{kJ\,mol^{-1}}$ and $K_p^\circ = 2.0 \times 10^{-5}$				
$T = 373.15$ K				
Phase	Gas	Gas	Gas	Gas
$\Delta_{298.15}^{373.15} H_m^\circ$ ($\mathrm{kJ\,mol^{-1}}$)	14.48	2.54 [27]	14.54 [8]	2.19 [27]
$\Delta_0^T S_m^\circ$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	416.8	196.4 [27]	409.4 [8]	205.2 [27]
$\Delta_r G_m^\circ = 26.8\,\mathrm{kJ\,mol^{-1}}$ and $K_p^\circ = 1.8 \times 10^{-4}$				

been considered:



(12)

The results of calculations of $\Delta_r G_m^\circ(T)$ and K_p° for the gaseous hydrolysis at $T = 298.15$ and 373.15 K (the average temperature of the reaction as described in [30]) are summarized in Table 11. Evidently, the equilibrium of the gas-phase hydrolysis of 1-bromoadamantane is strongly shifted towards the initial substances. However, in actual practice this reaction proceeds in aqueous solution (a mixture of aqueous HCl and dimethylformamide used as a solvent). The desired final product (1-hydroxyadamantane) is most likely to be solvated to a greater extent than 1-bromoadamantane. This results supposedly in the offset of the equilibrium towards the products making this process more preferable. The thorough thermodynamic analysis of the hydrolysis of 1-bromoadamantane in solution needs the study of the solvation process of both reactant and product.

5. Conclusions

The study of the thermodynamics of sublimation (the measurement of the sublimation enthalpy and the saturated vapour pressure) for 1-bromoadamantane and its thermodynamic properties in the ideal gaseous state was carried out in the present work. It is important to point out that good agreement was obtained by experimental and/or theoretical methods for the values of several different properties. The present results coupled with the thermodynamic properties of 1-bromoadamantane in the condensed state [5] constitute the valuable information for the analysis of different technological processes associated with this compound.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2005.06.043.

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