

Thermodynamic properties and the plastic crystal state of 2-methyl-2-adamantanol

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Received 2 May 2001; received in revised form 5 July 2001; accepted 30 July 2001

Abstract

The heat capacity investigation of 2-methyl-2-adamantanol in the condensed state was carried out in a vacuum adiabatic calorimeter between 5 and 310 K and in a scanning calorimeter of the heat bridge type between 300 and 530 K. It was found that 2-methyl-2-adamantanol has a phase transition into the “plastic” crystal state at 367.5 K. The thermodynamic characteristics of solid-to-solid phase transition and fusion ($T_{\text{fus}} = 488.8$ K) were obtained. According to the X-ray crystallography, the crII had the rhombic lattice of the space group $Pcc2$ and the crI had the cubic face-centered (fcc) lattice of the space group $F\bar{4}3c$. The lattice parameters were calculated. The entropy, the number of non-equivalent orientations and the energy difference between the “plastic” and the “basic” orientations of the molecules in the “plastic” crystal of 2-methyl-2-adamantanol were determined from the heat capacity. The contributions to the heat capacity and the entropy of the “plastic” crystal caused by the possible existence of the molecular dimers due to the hydrogen bonding were considered. The enthalpy of the hydrogen bond was determined from the shifts of the O–H valence vibration bands in the IR spectra of 2-methyl-2-adamantanol. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: 2-Methyl-2-adamantanol; Thermodynamic properties; Phase transition; Plastic crystals; Crystal structure

1. Introduction

The present work continues our investigations of thermodynamic properties of some cage hydrocarbons [1–3] and study of the influence of the molecular structure on the physical and chemical properties and the thermal behavior of the compounds existing in the “plastic” crystal state [4,5]. The heat capacity of 2-methyl-2-adamantanol was measured in a vacuum adiabatic calorimeter between 5 and 310 K and in a scanning calorimeter of the heat bridge type

between 300 and 530 K. The thermodynamic characteristics of the solid-to-solid transition and the fusion of this compound were evaluated. The structures of the high-temperature and the low-temperature crystalline phases of 2-methyl-2-adamantanol were investigated by the X-ray crystallography.

In our recent works [3,4] the way to estimate the number of the non-equivalent orientations n_{orient} and the mean energy difference between the “basic” and “plastic” orientations of the molecules $\Delta_{\text{orient}}H$ in the “plastic” crystalline phases of adamantane, some cage hydrocarbons and cyclohexane derivatives was suggested from the entropy and the heat capacity changes corresponding to the transitions from the “rigid” crystal (rig. cr) to the “plastic” crystal (pl. cr) of the compounds. In this work, the calculation of

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the values of n_{orient} and $\Delta_{\text{orient}}H$ for the “plastic” crystal of 2-methyl-2-adamantanol has been attempted taking into account the possibility of the existence of the molecular dimers due to the hydrogen bonding in this phase. The enthalpy of the hydrogen bond was determined from the shifts of the O–H valence vibration bands in the IR spectra of the compound under study.

2. Experimental

2-Methyl-2-adamantanol (Aldrich, with the mass fraction purity of 0.97) was purified by sublimation at $T = 308$ K and $P = 0.4$ kPa. The mass fraction purity of the sample thus refined was 0.9994 as determined by GLC.

The low-temperature heat capacity of 2-methyl-2-adamantanol in the condensed state between 5 and 310 K was measured in an automatic vacuum adiabatic calorimeter TAU-1 made by VNIIFTRI (Moscow) and already described [1,6,7]. The accuracy of the heat capacity measurements was verified in experiments with benzoic acid (K-1 grade, purity of not less than mass fraction 0.99995) [8,9] and highly purified copper (purity of not less than mass fraction 0.99995) [10]. The probable uncertainty of the molar heat capacity values $C_{s,m}$ was considered to be $\pm 4 \times 10^{-3} C_{s,m}$ over the temperature range 40–320 K. This uncertainty becomes larger at $T < 40$ K, and it achieves $\pm 2 \times 10^{-2} C_{s,m}$ at temperatures near 5 K. The sublimation corrections to the experimental heat capacities (less than 0.01% at 300 K) were negligibly small for 2-methyl-2-adamantanol as compared with the inaccuracy of the results and therefore the differences between the values of $C_{p,m}$ and $C_{s,m}$ were ignored.

The heat capacity of 2-methyl-2-adamantanol between 300 and 530 K was measured in an advanced and automated scanning calorimeter of the heat bridge type described earlier in details [11,12]. The calorimeter was calibrated by a high-purity copper (purity of not less than mass fraction 0.99995). The probable uncertainty of the heat capacity values was estimated to be about $\pm 2 \times 10^{-2} C_{s,m}$ [11]. The procedure of the transition temperature and the transition enthalpy determination was described earlier [13].

The enthalpy of sublimation for 2-methyl-2-adamantanol was measured in a differential heat-conducting

microcalorimeter of Calvet type MID-200 with special calorimetric cells, described earlier [14]. The saturated vapor pressure was determined by Knudsen integral effusion method. The apparatus construction and the measuring procedure were reported earlier [15,16].

The X-ray crystallographic study of the powder sample of 2-methyl-2-adamantanol was carried out in a X-ray diffractometer DRON-1.5 using cobalt as a source of X-rays. The values of angle 2θ were determined with the accuracy of not less than 0.01° . The X-ray study of the high-temperature crystalline phase of 2-methyl-2-adamantanol was performed using the high-temperature chamber GPVT-1500. The sample was loaded into the heat-resistant steel cell, the temperature of the cell was maintained constant with an accuracy of ± 0.5 K.

The IR absorption spectra for two crystalline phases of 2-methyl-2-adamantanol and 2-methyl-2-adamantanol, dissolved in CCl_4 , in the wavenumber range (4000–3000) cm^{-1} were recorded with the “Karl Zeiss” Specord 75 IR spectrometer. The tablets obtained by the pressing of the crystalline sample and powder KBr together (the mass fraction of 2-methyl-2-adamantanol in a tablet was about 0.005) and the thin films of liquid between KBr plates were studied. The IR spectra for the high-temperature crystalline phase of 2-methyl-2-adamantanol was registered using the “Karl Zeiss” thermostatic chamber. The temperature was measured with integrated {Fe-to-(0.52Cu + 0.48Ni)} thermocouple and was kept constant with an accuracy of ± 2 K.

3. Thermodynamic properties and crystal structure of 2-methyl-2-adamantanol

The molecular structure of 2-methyl-2-adamantanol is given in Fig. 1.

The temperature dependence of the heat capacity of the compound in the range of (5–530 K) is shown in Fig. 2.

It was found that the heat capacity of 2-methyl-2-adamantanol did not follow the Debye law in the low-temperature range in spite of the majority of the compounds. To extrapolate the heat capacity of the crII to $T < 5.6$ K, the experimental heat capacities between $T = (5.6$ and 12 K) were approximated by the sum of Debye and Einstein contributions using

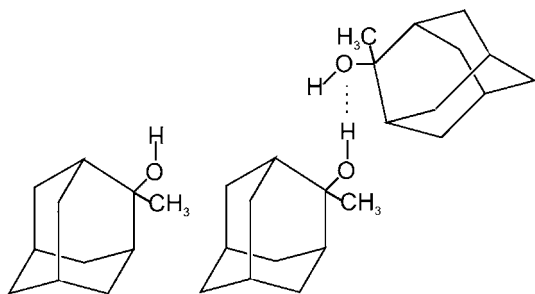


Fig. 1. The molecular structures of 2-methyl-2-adamantanol in the monomeric and the dimeric forms.

three characteristic Debye temperatures ($\Theta_{D1} = \Theta_{D2} = 140.1$ K, $\Theta_{D3} = 79.8$ K) and one characteristic Einstein temperature ($\Theta_E = 58.6$ K). Root mean square was 1.1% (Fig. 3). The entropy and the reduced enthalpy of 2-methyl-2-adamantanol at 5 K (Table 1) were calculated from the extrapolated values of the heat capacity.

The heat capacity temperature dependencies for the crII from 300 to 367.5 K, for the crI from 367.5 to 488.8 K and for the liquid phase of 2-methyl-2-adamantanol from 488.8 to 530.0 K, respectively were assumed to be expressed by

$$C_{s,m}(T) \text{ (J K}^{-1} \text{ mol}^{-1}) = (14.23 \pm 1.23) + (0.6738 \pm 0.0037)(T) \text{ (K)} \quad (1)$$

$$C_{s,m}(T) \text{ (J K}^{-1} \text{ mol}^{-1}) = (308.6 \pm 4.6) + (0.1461 \pm 0.0103)(T) \text{ (K)} \quad (2)$$

$$C_{s,m}(T) \text{ (J K}^{-1} \text{ mol}^{-1}) = (220.0 \pm 3.7) + (0.3622 \pm 0.0298)(T) \text{ (K)} \quad (3)$$

The smoothed values of the molar heat capacity and the standard thermodynamic functions of 2-methyl-2-

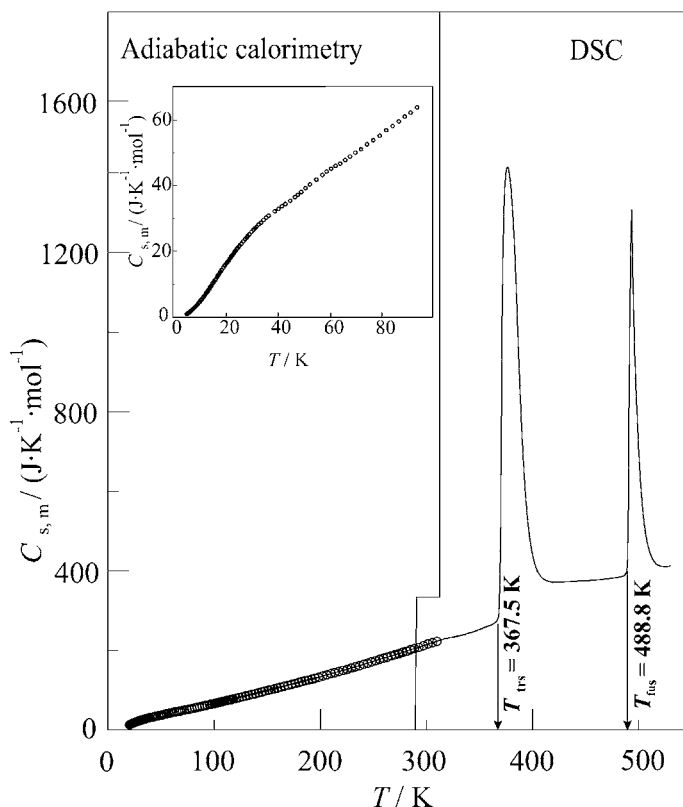


Fig. 2. The temperature dependence of the heat capacity in the condensed state for 2-methyl-2-adamantanol.

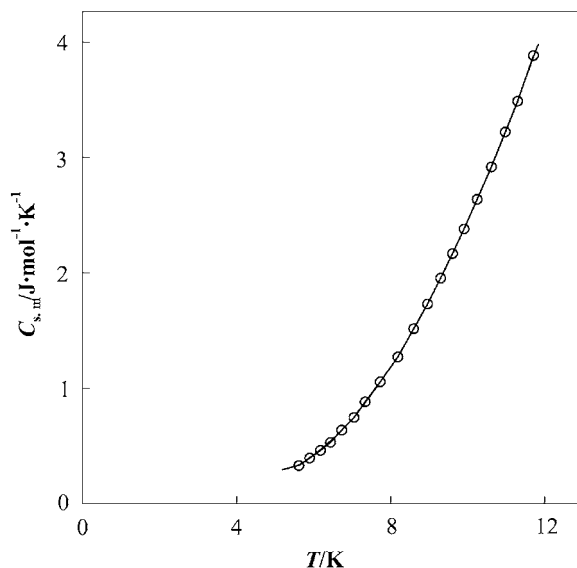


Fig. 3. Dependence of $C_{s,m}$ vs. T for 2-methyl-2-adamantanol in the low temperature range (circles are the experimental values of the molar heat capacity and the curve is the smoothed values of the molar heat capacity, obtained using $\Theta_{D1} = \Theta_{D2} = 140.1$ K and $\Theta_{D3} = 79.8$ K and $\Theta_E = 58.6$ K).

adamantanol in the condensed state are given in Table 1. Some thermodynamic characteristics of 2-methyl-2-adamantanol are represented in Table 2.

It was found that 2-methyl-2-adamantanol has one solid-to-solid phase transition at 367.5 K with the entropy of $\Delta_{\text{crII}}^{\text{crI}}S^\circ = (50.8 \pm 1.0 \text{ J K}^{-1} \text{ mol}^{-1})$ which is much higher than the entropy of fusion $\Delta_{\text{crI}}^{\text{l}}S^\circ = (15.1 \pm 0.3 \text{ J K}^{-1} \text{ mol}^{-1})$. As noted in [4] one of the criteria for the compound to undergo the transition into the “plastic” crystal state is $\Delta_{\text{trs}}S/\Delta_{\text{fus}}S \geq 1$. Based on this criterion, the crI of 2-methyl-2-adamantanol ($\Delta_{\text{trs}}S/\Delta_{\text{fus}}S = 3.4$) which exists in the range of 367.5–488.8 K can be assigned to the “plastic” crystals. The essential decrease of the density at the transition crII \rightarrow crI and the high-temperature crystalline phase having the cubic type lattice can be, probably, another criterion of the “plastic” crystal formation.

To clarify the structures of the crystals of 2-methyl-2-adamantanol, the X-ray diffraction study for the high-temperature and low-temperature crystalline phases of the compound was carried out (Fig. 4). It was found that the crII had the rhombic lattice of the space group $Pcc2$ ($a = (9.47 \pm 0.01) \times 10^{-10}$ m,

Table 1

Molar thermodynamic functions of 2-methyl-2-adamantanol

T (K)	$C_{p,m}/R$	$\Delta_0^T H_m^\circ/RT$	$\Delta_0^T S_m^\circ/R$	Φ_m°/R
Crystal II				
5	0.0248	0.0066	0.0088	0.0022
10	0.294	0.0678	0.0878	0.0201
20	1.585	0.481	0.656	0.175
30	2.875	1.073	1.553	0.480
40	3.794	1.648	2.517	0.869
50	4.504	2.147	3.439	1.292
60	5.252	2.603	4.327	1.724
70	5.911	3.029	5.187	2.158
80	6.578	3.430	6.019	2.589
90	7.288	3.819	6.834	3.015
100	8.022	4.203	7.640	3.437
120	9.543	4.965	9.236	4.271
140	11.12	5.731	10.82	5.094
160	12.74	6.505	12.41	5.910
180	14.40	7.290	14.01	6.721
200	16.12	8.086	15.62	7.530
220	17.91	8.897	17.24	8.339
240	19.77	9.725	18.87	9.148
260	21.72	10.57	20.53	9.960
273.15	23.03	11.14	21.64	10.50
280	23.73	11.44	22.22	10.78
298.15	25.60	12.24	23.76	11.52
300	25.79	12.33	23.92	11.59
350	30.10	14.57	28.24	13.66
367.5	31.51	15.35	29.74	14.39
Crystal I				
367.5	43.57	21.45	35.85	14.39
400	44.15	23.27	39.56	16.29
450	45.02	25.64	44.82	19.18
488.8	45.71	27.21	48.57	21.36
Liquid				
488.8	47.76	29.02	50.38	21.36
500	48.25	29.44	51.47	22.02
530	49.55	30.55	54.32	23.77

$b = (10.70 \pm 0.01) \times 10^{-10}$ m, $c = (9.25 \pm 0.01) \times 10^{-10}$ m, $V_0 = (937.29 \pm 0.03) \times 10^{-30}$ m³, $z = 4$) and the calculated X-ray density was $D_x = 1.18 \times 10^3 \text{ kg m}^{-3}$. The crI has the fcc lattice of the space group $F\bar{4}3c$ ($a = (10.28 \pm 0.02) \times 10^{-10}$ m, $V_0 = (1086.37 \pm 0.03) \times 10^{-30}$ m³, $z = 4$) and the calculated X-ray density is $D_x = 1.02 \times 10^3 \text{ kg m}^{-3}$. Thus, the X-ray density of 2-methyl-2-adamantanol decrease abruptly (approximately by 15%) at the solid-to-solid phase transition. The obtained results support the conclusion that the crI of 2-methyl-2-adamantanol is the “plastic” crystal.

Table 2
Some thermodynamics characteristics of 2-methyl-2-adamantanol

Property	Value
T_{rs}/K	367.5 ± 0.1
$\Delta_{trs}H_m^\circ$ (J mol ⁻¹)	18659 ± 371
$\Delta_{trs}S_m^\circ$ (J K ⁻¹ mol ⁻¹)	50.77 ± 1.02
$\Delta_{crlI}^{crl}C_s(T_{trs})$ (J K ⁻¹ mol ⁻¹)	100.3 ± 2.0
T_{fus} (K)	488.8 ± 0.1
$\Delta_{fus}H_m^\circ$ (J mol ⁻¹)	7381 ± 148
$\Delta_{fus}S_m^\circ$ (J K ⁻¹ mol ⁻¹)	15.10 ± 0.30
$\Delta_{crl}^I C_s(T_{fus})$ (J K ⁻¹ mol ⁻¹)	17.06 ± 0.34
$T = 298.15$ K	Crystal II
C_p (J K ⁻¹ mol ⁻¹)	212.9 ± 0.9
$(\Delta_0^T H_m^\circ / T)$ (J K ⁻¹ mol ⁻¹)	101.8 ± 0.4
$\Delta_0^T S_m^\circ$ (J K ⁻¹ mol ⁻¹)	197.6 ± 0.8
Φ_m° (J K ⁻¹ mol ⁻¹)	95.8 ± 0.4

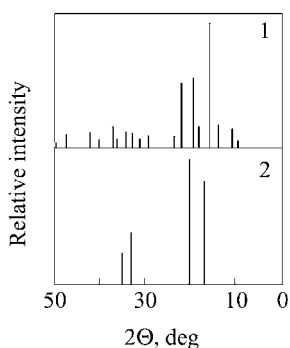


Fig. 4. X-ray image of 2-methyl-2-adamantanol: curve 1 is for the crII (“rigid” crystal) at 295 K; curve 2 is for the crI (“plastic” crystal) at 423 K.

4. The energy states of the molecules in the “plastic” crystal of 2-methyl-2-adamantanol

It was shown in our recent works [3,4] that the entropy and the heat capacity changes corresponding to the transition from the “rigid” crystal to the “plastic” crystal can be represented as the following sums:

$$\Delta_{rig.cr}^{pl.cr} C_s = \Delta_v C_s + \Delta_{conf} C_s + \Delta_{orient} C_s \quad (4)$$

$$\Delta_{rig.cr}^{pl.cr} S = \Delta_v S + \Delta_{conf} S + \Delta_{orient} S \quad (5)$$

where $\Delta_v C_s$ and $\Delta_v S$ are the volume-change contributions, $\Delta_{conf} C_s$ and $\Delta_{conf} S$ are the conformational

contributions, $\Delta_{orient} C_s$ and $\Delta_{orient} S$ are the contributions due to the orientational disordering of the molecules in the “plastic” crystal state.

The heat capacity change at the “rigid” crystal-to-“plastic” crystal transition of 2-methyl-2-adamantanol ($\Delta_{rig.cr}^{pl.cr} C_s = 100.3$ J K⁻¹ mol⁻¹) is much higher than the corresponding value for adamantane ($\Delta_{rig.cr}^{pl.cr} C_s = 8.9$ J K⁻¹ mol⁻¹ [3] from the data [17]). It is probably caused by the existence of the much greater number of the non-equivalent molecular orientations in the “plastic” crystal of 2-methyl-2-adamantanol with respect to the corresponding value for adamantane due to the fact that the molecules of 2-methyl-2-adamantanol have the much lower number of symmetry ($\sigma = 1$) than the molecules of adamantane ($\sigma = 12$). Furthermore, if the molecules of 2-methyl-2-adamantanol form dimers due to the hydrogen bonding and the dimeric (*D*) and the monomeric (*M*) molecular forms are in equilibrium (this equilibrium is denoted by $D \rightleftharpoons 2M$) in the “plastic” crystalline phase, then the change of the equilibrium fraction of the monomers with the temperature rise should be accompanied by the additional contribution to the heat capacity change under study. The number of the non-equivalent orientations of the molecules in the “plastic” crystal of 2-methyl-2-adamantanol can also increase essentially due to the presence of the monomers and the dimers in this phase.

To clear up the question whether the hydrogen bonds between the molecules are available in the “rigid” and “plastic” crystals of 2-methyl-2-adamantanol, the IR spectra study over the wavenumber range (4000–3000) cm⁻¹ was carried out for the both crystalline phases and also for the 0.1 M solution of 2-methyl-2-adamantanol in CCl₄. The IR spectra of the “rigid” crystal (crII) and of the solution were recorded at 293 K and the IR spectrum of the “plastic” crystal (crI) was recorded at 423 K and all the spectra obtained are shown in Fig. 5.

As can be seen from the IR spectra of the “rigid” crystal and 0.1 M solution of 2-methyl-2-adamantanol in CCl₄, only the molecular dimers with the O–H valence vibration band of 3400 cm⁻¹ exist in the “rigid” crystal. The molecules of 2-methyl-2-adamantanol in the solution are partly associated to form the dimers. It is manifested as two well separated bands of the O–H valence vibration, namely, the narrow band of 3617 cm⁻¹ for the monomers and

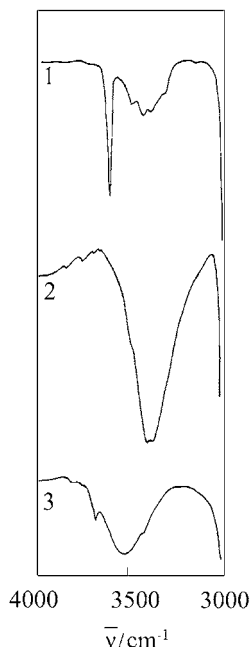


Fig. 5. The IR spectra of 2-methyl-2-adamantanol: curve 1 is for 0.1 M solution in CCl_4 at 293 K; curve 2 is for the crII (“rigid” crystal) at 293 K; curve 3 is for the crI (“plastic” crystal) at 423 K.

the broad band with the maximum of 3425 cm^{-1} for the dimers.

In the IR spectrum of the “plastic” crystal of 2-methyl-2-adamantanol (curve 3 in Fig. 5):

- the band of the valence vibration of the “bounded” hydroxyl group with the maximum of 3500 cm^{-1} is shifted to the region of the higher wavenumbers as compared with the “rigid” crystal and this fact allows to conclude that the energy of the hydrogen bond in the “plastic” crystal of 2-methyl-2-adamantanol is essentially smaller than the appropriate value in the “rigid” crystal;
- in addition, there is a weak signal of the narrow band corresponding to the valence vibration of the “free” hydroxyl group with the maximum of 3617 cm^{-1} and this fact indicates that the monomers exist in the high-temperature crystalline phase of 2-methyl-2-adamantanol.

It can be suggested from the IR spectra data that the dimeric and the monomeric forms of the molecules are in a dynamic equilibrium in the “plastic” crystal of 2-methyl-2-adamantanol. So, the contributions to the

heat capacity and the entropy ($\Delta_{\text{dis}}C_s$ and $\Delta_{\text{dis}}S$, respectively) caused by the existence of a such equilibrium in the “plastic” crystal should be taken into account when the interpretation of the energy states of the molecules in the “plastic” crystalline phase of 2-methyl-2-adamantanol is carried out.

Considering the parameters mentioned above, the transition into the “plastic” crystal state for 2-methyl-2-adamantanol can be represented as the following sums:

$$\Delta_{\text{rig. cr}}^{\text{pl. cr}} C_s = \Delta_v C_s + \Delta_{\text{conf}} C_s + \Delta_{\text{dis}} C_s + \Delta_{\text{orient}} C_s \quad (6)$$

$$\Delta_{\text{rig. cr}}^{\text{pl. cr}} S = \Delta_v S + \Delta_{\text{conf}} S + \Delta_{\text{dis}} S + \Delta_{\text{orient}} S \quad (7)$$

4.1. The volume-change contributions $\Delta_v C_s$ and $\Delta_v S$ at the phase transition

Since the (V_m, T) -isobars of the organic crystals are nearly linear [4] and, hence, $(\partial^2 V / \partial T^2) \approx 0$, the volume-change contribution $\Delta_v C_s$ may be ignored when considering the solid-to-solid phase transition under study [18].

The volume-change contribution to the entropy of the phase transition can be calculated on the basis of (p, V_m, T) data by the following equation:

$$\begin{aligned} \Delta_v S &= \int_{V_1}^{V_2} \left(\frac{\partial p}{\partial T} \right)_V dV = \int_{V_1}^{V_2} (\beta_V(V)) dV \\ &= \bar{\beta}_V \Delta_{\text{trs}} V \end{aligned} \quad (8)$$

where V_1 and V_2 are the molar volumes of the “rigid” crystal and the “plastic” crystal, respectively, at the temperature of the solid-to-solid transition, $\bar{\beta}_V$ is the mean pressure coefficient for the “plastic” crystal in the range from V_1 to V_2 , and $\Delta_{\text{trs}} V = V_2 - V_1$. There are no experimental data for the estimation of $\bar{\beta}_V$. It was shown [4] that the ratio $(\Delta_v S / \Delta_{\text{rig. cr}}^{\text{pl. cr}} S) \approx 0.4$ is the average value for the “rigid” crystal-to-“plastic” crystal transitions of some cyclohexane derivatives. This value was used to estimate the volume-change contribution to the entropy change at the transition into the “plastic” crystal state for 2-methyl-2-adamantanol.

4.2. The conformational contributions $\Delta_{\text{conf}} C_s$ and $\Delta_{\text{conf}} S$ at the phase transition

When these contributions were calculated, the mixing of the conformers formed by the rotation of the

hydroxyl top was considered in the monomers only. The contributions caused by the conformational conversions in the dimeric forms of the molecules were close to zero since the energy differences between the conformers of the dimers were estimated to be too great. The energy differences between the rotational isomers of the monomers of 2-methyl-2-adamantanol were close to zero according to the calculations by the molecular mechanics method with the MM3 force field. So, the conformational contribution $\Delta_{\text{conf}}C_s$ was assumed to be equal to zero.

The conformational contribution to the entropy of the phase transition can be determined by the equation:

$$\Delta_{\text{conf}}S = [R \ln(3)]x_m \quad (9)$$

where x_m is the equilibrium molar fraction of the monomers. The way to calculate the value of x_m is described below.

4.3. The contributions to the heat capacity $\Delta_{\text{dis}}C_s$ and the entropy changes $\Delta_{\text{dis}}S$ caused by the existence of the equilibrium $D \rightleftharpoons 2M$ in the “plastic” crystal

The contribution to the heat capacity due to the existence of the equilibrium $D \rightleftharpoons 2M$ can be calculated by the equation:

$$\Delta_{\text{dis}}C_s = \frac{\Delta_r H}{2} \left(\frac{\partial x_m}{\partial T} \right) \quad (10)$$

where $\Delta_r H$ is the enthalpy of the reaction $D \rightarrow 2M$, T is the temperature.

Since for each n mole of the monomers forming in the reaction $D \rightleftharpoons 2M$ there is $(0.5(1-n))$ mole of the dimers, the equilibrium molar fraction of the monomers is:

$$x_m = \frac{n}{0.5(1+n)} \quad (11)$$

Then, taking into account the Eqs. (10) and (11), the following equation can be obtained:

$$\Delta_{\text{dis}}C_s = \frac{\Delta_r H}{4} \frac{\Delta_r H}{RT^2} a \frac{[4+a]^{-1}([4+a]^{-1}a)}{(a[4+a]^{-1})^{0.5}} \quad (12)$$

where $a = \exp(-\Delta_r G/RT)$, $\Delta_r G$ is the Gibbs energy of the reaction $D \rightarrow 2M$.

The value of $\Delta_r H$ (kJ mol^{-1}) can be estimated from the IR spectra data according to the empirical rules of Iogansen for alcohols [19,20]:

$$\Delta_r H = 4.184 \left(\frac{\Delta\nu}{9.3} \right)^{0.5} \quad (13)$$

or

$$\Delta_r H = 4.184 \times 0.33(\Delta\nu - 40)^{0.5} \quad (14)$$

where $\Delta\nu$ (cm^{-1}) is the difference between the values of wavenumbers for the “free” and the “bounded” hydroxyl groups. The values of $\Delta_r H$ obtained from Eqs. (13) and (14) for the “rigid” and the “plastic” crystals of 2-methyl-2-adamantanol are presented in Table 3. The change of the enthalpy of the reaction $D \rightarrow 2M$ at the temperature decrease from 423 K to T_{trs} could be ignored because this change is much less than a probable error of the estimation of the value of $\Delta_r H$. So, it can be assumed that $\Delta_r H(367.5 \text{ K}) = (13.5 \pm 1.3) \text{ kJ mol}^{-1}$ for the “plastic” crystal of 2-methyl-2-adamantanol.

The contribution to the entropy caused by the equilibrium between the monomers and the dimers in the “plastic” crystal can be calculated by the equation:

$$\Delta_{\text{dis}}S = \frac{\Delta_r S x_m}{2} \quad (15)$$

where $\Delta_r S$ is the entropy of the reaction $D \rightarrow 2M$.

To estimate the value of $\Delta_r S$, the saturated vapor pressure $P_{\text{sat}}(298.15 \text{ K}) = (0.293 \pm 0.015) \text{ Pa}$ and the enthalpy of sublimation of 2-methyl-2-adamantanol $\Delta_{\text{crII}}^{\text{g}}H(298.15 \text{ K}) = (9.14 \pm 0.7) \text{ kJ mol}^{-1}$ were determined. The fraction of the dimers was estimated to be negligible in the equilibrium gas phase at the saturated vapor pressure. What this means is the process of sublimation is accompanied by the almost

Table 3
The values of $\Delta_r H$ for 2-methyl-2-adamantanol calculated from the IR spectra data

Phase	T (K)	$\Delta\nu$ (cm^{-1})	$\Delta_r H$ (kJ mol^{-1}) ^a	$\Delta_r H$ (kJ mol^{-1}) ^b	$\langle \Delta_r H \rangle$ (kJ mol^{-1})
crII	293	217	20.2	18.4	19.3 ± 0.9
crI	423	117	14.8	12.1	13.5 ± 1.3

^a Calculated by Eq. (13).

^b Calculated by Eq. (14).

Table 4

The standard molar entropies of sublimation (all entropies values are in $\text{J K}^{-1} \text{mol}^{-1}$) at $T = 298.15 \text{ K}$ for some hydrocarbons and 2-methyl-2-adamantanol

Compound	$A_{\text{subl}}S$	P_{sat} (Pa)	$A_{\text{subl}}S^\circ$	$\Delta_{\text{rig.cr}}^{\text{pl.cr}}S^\circ$	$\Delta_{\text{rig.cr}}^{\text{g}}S^\circ$	σ	$\Delta_{\text{rig.cr}}^{\text{g}}S_{\text{eff}}^\circ$	Reference
Bicyclo[2.2.2]octane	161.0	444.9	115.9	27.9	143.8	6	158.7	[21]
Adamantane	197.1	18.9	125.7	16.2	141.9	12	162.6	[3]
Naphthalene	243.2	10.6	167.0	0.0	167.0	4	178.5	[22]
Pentacycloundecane	187.3	37.0	121.5	29.57	151.1	1	151.1	[2]
Heptacyclotetradecane	267.6	0.85	170.4	0	170.4	4	181.9	[1]
2-Methyl-2-adamantanol	306.6	0.293	200.5	0	200.5	1	200.5	This work

complete dissociation of the dimers of 2-methyl-2-adamantanol. The standard entropy of sublimation for the “rigid” crystal of 2-methyl-2-adamantanol is $\Delta_{\text{rig.cr}}^{\text{g}}S^\circ(298.15 \text{ K}) = (200.5 \pm 0.9) \text{ J K}^{-1} \text{mol}^{-1}$ from the data obtained. The standard entropies of sublimation at 298.15 K were also obtained for the hydrocarbons having no hydrogen bonds and, therefore, the processes of sublimation for these compounds are accompanied by the transition of the molecules from the crystal state into the gas state only. If the compound is in the “plastic” crystal state at $T = 298.15 \text{ K}$, then the value of $\Delta_{\text{rig.cr}}^{\text{pl.cr}}S^\circ$ was added to the value of $\Delta_{\text{pl.cr}}^{\text{g}}S^\circ(298.15 \text{ K})$ to determine the standard entropy of sublimation for the “rigid” crystal. The obtained results are given in Table 4. The values of the effective standard entropy of sublimation $\Delta_{\text{rig.cr}}^{\text{g}}S_{\text{eff}}^\circ$ taking into account the number of symmetry of the molecules (σ) in the gas state

$$\Delta_{\text{rig.cr}}^{\text{g}}S_{\text{eff}}^\circ(298.15 \text{ K}) = \Delta_{\text{rig.cr}}^{\text{g}}S^\circ(298.15 \text{ K}) + R \ln(\sigma) \quad (16)$$

are also presented in Table 4.

As can be seen from Table 4, the value of $\Delta_{\text{rig.cr}}^{\text{g}}S_{\text{eff}}^\circ(298.15 \text{ K})$ is approximately constant and is $(166 \pm 16) \text{ J K}^{-1} \text{mol}^{-1}$ on the average for the compounds having no hydrogen bonds in the crystalline state. The difference between the value of

$\Delta_{\text{rig.cr}}^{\text{g}}S_{\text{eff}}^\circ(298.15 \text{ K})$ for 2-methyl-2-adamantanol and the mean value of the effective standard entropy of sublimation for hydrocarbons is equal to $34 \text{ J K}^{-1} \text{mol}^{-1}$ and was used as the estimated value of $\Delta_{\text{r}}S$ for 2-methyl-2-adamantanol.

4.4. The contributions to the heat capacity ($\Delta_{\text{orient}}C_s$) and the entropy ($\Delta_{\text{orient}}S$) changes due to the reorientations of the molecules in the plastic crystal

The values of the all above discussed contributions to the heat capacity and the entropy changes corresponding to the “rigid” crystal-to-“plastic” crystal transition of 2-methyl-2-adamantanol were calculated according to the foregoing assumptions at T_{trs} and are given in Table 5. The values of $\Delta_{\text{orient}}C_s$ and $\Delta_{\text{orient}}S$ can be determined from the relations (6) and (7) in the following way:

$$\Delta_{\text{orient}}C_s = \Delta_{\text{rig.cr}}^{\text{pl.cr}}C_s - \Delta_{\text{dis}}C_s \quad (17)$$

$$\begin{aligned} \Delta_{\text{orient}}S &= (\Delta_{\text{rig.cr}}^{\text{pl.cr}}S - \Delta_{\text{v}}S) - \Delta_{\text{conf}}S - \Delta_{\text{dis}}S \\ &= 0.6\Delta_{\text{tr}}S - R \ln(3)x_m - \frac{\Delta_{\text{r}}Sx_m}{2} \end{aligned} \quad (18)$$

From the data of Table 5, it was obtained that $\Delta_{\text{orient}}C_s = 86.9 \text{ J K}^{-1} \text{mol}^{-1}$ and $\Delta_{\text{orient}}S = 20.3 \text{ J K}^{-1} \text{mol}^{-1}$ for 2-methyl-2-adamantanol.

Table 5

The contributions to the heat capacity and the entropy changes at the phase transition from the “rigid” crystal to the “plastic” crystal 2-methyl-2-adamantanol at $T = 367.5 \text{ K}$

	Transition crII \rightarrow crI	Volumetric changes ($\text{J K}^{-1} \text{mol}^{-1}$)	Conformational contribution ($\text{J K}^{-1} \text{mol}^{-1}$)	Dissociation contribution ($\text{J K}^{-1} \text{mol}^{-1}$)	Orientational contribution ($\text{J K}^{-1} \text{mol}^{-1}$)
Heat capacity	100.3	0	0	13.4	86.9
Entropy	50.8	20.3	3.6	6.6	20.3

The model of the energy states of the molecules in the “plastic” crystals proposed in our recent works [3,4] allow to the interpretation of the values of $\Delta_{\text{orient}}S$ and $\Delta_{\text{orient}}C_s$ simultaneously. According to this model, in the “plastic” crystal there is the “basic” orientation of the molecules with the energy of H_{bas} which is close to the energy of the orientation of the molecules in the “rigid” crystal and also there is a great number of the “plastic” orientations with the energies which are very close to each other and higher than the value of H_{bas} (Fig. 6).

The contributions to the heat capacity and the entropy changes arising from the orientational disordering of the molecules in the “plastic” crystalline phase can be determined from equations [3]:

$$\Delta_{\text{orient}}C_s = \frac{1}{RT^2} (n_{\text{orient}} - 1) x_{\text{bas}} x_{\text{plast}} (\Delta_{\text{orient}}H)^2 \quad (19)$$

$$\Delta_{\text{orient}}S = -R [x_{\text{bas}} \ln x_{\text{bas}} + (n_{\text{orient}} - 1) x_{\text{plast}} \ln x_{\text{plast}}] \quad (20)$$

where $\Delta_{\text{orient}}H = (H_{\text{plast}})_{\text{mean}} - H_{\text{bas}}$ is the mean energy difference between the “plastic” and the “basic” molecular orientations; n_{orient} is the number of the non-equivalent orientations of the molecules in

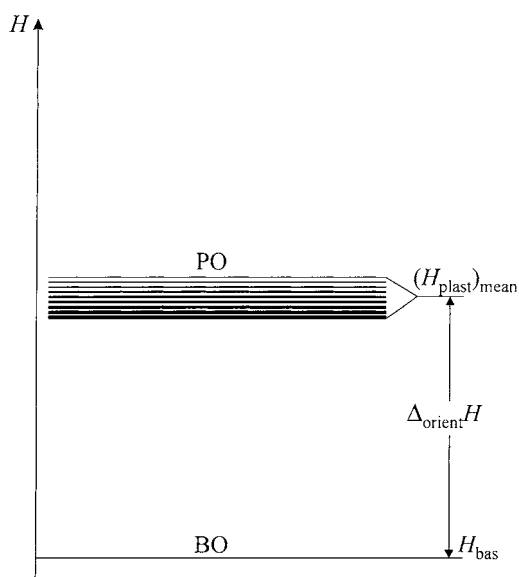


Fig. 6. The model of the energy states of the molecules in the “plastic” crystal state for 2-methyl-2-adamantanol. PO are the “plastic” orientations of the monomeric and dimeric molecules and BO is the “basic” orientation of molecules.

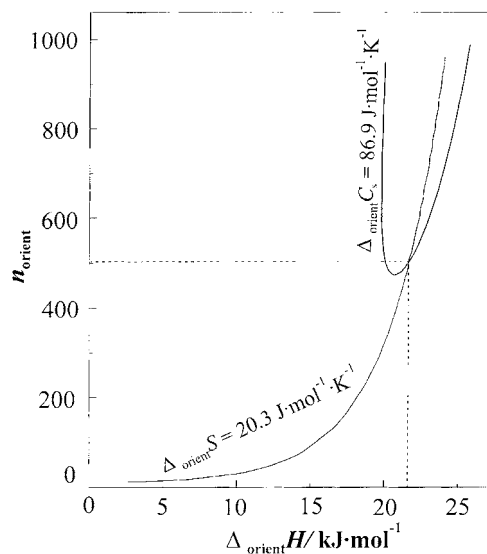


Fig. 7. The number of non-equivalent orientations of the molecules in the “plastic” crystal of 2-methyl-2-adamantanol (n_{orient}) vs. the mean energy difference between the “plastic” and the “basic” molecular orientations ($\Delta_{\text{orient}}H$) at 367.5 K for the values of $\Delta_r S = 34 \text{ J K}^{-1} \text{ mol}^{-1}$, $\Delta_{\text{orient}}S = 20.3 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta_{\text{orient}}C_s = 86.9 \text{ J K}^{-1} \text{ mol}^{-1}$.

the “plastic” crystal; x_{bas} is the molar fraction of the molecules having the “basic” orientation; x_{plast} is the molar fraction of the molecules having one of the “plastic” orientations.

There is a set of the solutions of Eqs. (19) and (20) separately for the values of $\Delta_{\text{orient}}C_s = 86.9 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta_{\text{orient}}S = 20.3 \text{ J K}^{-1} \text{ mol}^{-1}$ [7]. The values of $n_{\text{orient}} = 505$ and $\Delta_{\text{orient}}H = 21.7 \text{ kJ mol}^{-1}$ were obtained as the only result of the solution for the system of Eqs. (19) and (20) using the above-mentioned values of $\Delta_{\text{orient}}C_s$ and $\Delta_{\text{orient}}S$ (Fig. 7). Both the number of the non-equivalent orientations of the molecules and the energy difference $\Delta_{\text{orient}}H$ for 2-methyl-2-adamantanol are much greater than the corresponding values for adamantane ($n_{\text{orient}} = 5$ and $\Delta_{\text{orient}}H = 3.8 \text{ kJ mol}^{-1}$ [3]). It seems reasonable because the molecules of 2-methyl-2-adamantanol have the much lower symmetry number for the overall rotation ($\sigma = 1$) than the adamantane molecules ($\sigma = 12$) and can form a variety of ensembles of the monomeric and dimeric orientations. It seems also justified that the value of $\Delta_{\text{orient}}H = 21.7 \text{ kJ mol}^{-1}$ is higher than the energy of the hydrogen bond of $\Delta_r H \approx 13.5 \text{ kJ mol}^{-1}$ estimated from the IR data.

5. Conclusion

It was found that 2-methyl-2-adamantanol, like other derivatives of the cage hydrocarbons, exists in the “plastic” crystal state over the wide temperature interval. The molecules of 2-methyl-2-adamantanol are completely associated to form the dimers in the “rigid” crystal state. The energy of the hydrogen bond decrease at the transition from the “rigid” crystal to the “plastic” crystal and the dimers and the monomers seem to be in the equilibrium in the “plastic” crystal. As a result, the heat capacity change corresponding to the transition of 2-methyl-2-adamantanol into the orientationally disordered crystalline phase increases to high value and it can be interpreted by the essentially great number of the non-equivalent molecular orientations with the higher energies than for adamantane due to the low symmetry number of the molecules of 2-methyl-2-adamantanol and the existence of the orientational ensembles forming by the monomers and the dimers in the “plastic” crystal.

Acknowledgements

The authors are grateful to V.N. Naumenko and A.S. Sobesky for the help in the registration of IR spectra and the performing of X-ray analysis, respectively.

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