ELSEVIER

Thermochimica Acta 292 (1997) 19–29

thermochimica
acta

Thermodynamic properties of 1-methylcyclopentanol and 1-chloro-1-methylcyclopentane in the ideal gas state

A.V. Blokhin, G.J. Kabo*, A.A. Kozyro, L.S. Ivashkevich, A.P. Krasulin, V.V. Diky, Yu.V. Maksimuk

Department of Chemistry, Belorussian State University, Leningradskaya 14, Minsk 220080, Belarus

Received 22 July 1996; accepted 11 November 1996

Abstract

The enthalpies of evaporation, the saturated vapor pressures of 1-methylcyclopentanol (I) and 1-chloro-1-methylcyclopentane (II) and the energy of combustion of crystal I were measured. IR and Raman spectra of both compounds were recorded and vibrational analyses were made. Thermodynamic functions of I and II in the ideal gas state were calculated by the statistical thermodynamics methods. In order that the experimental and calculated entropies of gaseous 1,1-ClMeCP agree, it is necessary to determine the contribution of pseudorotation as the contribution of motion with potential function $V(\phi) = \{5800 - 3060\cos(\phi) - 2740\cos(2\phi)\}\,\mathrm{J\,mol^{-1}}$ and pseudorotational moment of inertia $15.24\times10^{-40}\,\mathrm{g\,cm^2}$. The molecular rotation in the plastic crystal state of II is discussed. © 1997 Elsevier Science B.V.

Keywords: 1-Methylcyclopentanol; 1-Chloro-1-methylcyclopentane; Thermodynamic properties; Plastic crystals; Vibrational spectra

1. Introduction

The present work continues our investigations of thermodynamic properties of some cyclopentane derivatives [1,2], in order to study the influence of ring inversion on physical and chemical properties of substances. Heat capacities and enthalpies of transitions for 1-methylcyclopentanol (1-MeCPol) and 1-chloro-1-methylcyclopentane (1,1-ClMeCP) in the condensed state between 5 and 315 K were reported in [3]. To obtain the experimental entropies of these gaseous compounds, their enthalpies of evaporation and saturated vapor pressures were measured in this work. The enthalpy of combustion of crystal 1-MeCPol and the standard enthalpies of formation of crystal and gaseous 1-MeCPol were also determined. IR and Raman spectra of both compounds were recorded and vibrational analyses were made. Thermodynamic functions of 1-MeCPol and 1,1-ClMeCP in the ideal gas state were calculated by the statistical thermodynamics methods. In order that the experimental and calculated entropies of gaseous 1,1-ClMeCP agree, it is necessary to determine the contribution of pseudorotation as the contribution of motion with potential function $V(\phi) = \{5800 - 3060\cos(\phi) - 2740\cos(2\phi)\}\,\mathrm{J\,mol^{-1}}$ and pseudorotational moment of inertia $15.24\times10^{-40}\,\mathrm{g\,cm^2}$. It was shown by the statistical calculations that prohibitions of internal rotation and pseudorotation are removed at transition of 1,1-ClMeCP into the plastic crystals and a hindered general rotation of molecules in nodes of crystal lattice exists in the plastic phase.

---

*Corresponding author. Fax: +7 (0172) 265567.

PII S0040-6031(96)03107-3

2. Experimental

The samples of 1-MeCPol and 1,1-ClMeCP were synthesized by the methods given in [3]. The purities of 1-MeCPol and 1,1-ClMeCP were 99.96% and 99.94%, respectively, according to GLS.

The sublimation and vaporization enthalpies were determined in a differential heat-conducting microcalorimeter of Calvet type MID-200 with special calorimetric cells, described earlier [4]. The modernized MID-200 included a voltmeter with limits of measurements between 1×10^{-9} and 2 V and relaxation time between 2 and 30 s and also an IBM PC. The samples were placed in hermetic cells of stainless steel supplied with a nickel membrane. After preliminary thermostating of the calorimeter the membrane was pierced by a special demountable rod and the heating flux needed for evaporation was recorded. The calorimeter was calibrated by sublimation of benzoic acid (K-1) and naphthalene and by vaporization of *n*-decane and bidistillated water. As a result, we found that the uncertainty of evaporation enthalpy measurements did not exceed ±0.5%.

The saturated vapor pressures of compounds were determined by the integral effusion Knudsen method. The temperature was controlled to within ±0.02 K and weighting was reproducible to within $\pm1\times10^{-5}$ g. The sample was located in a stainless steel chamber, which was sealed with a teflon gasket. Membranes of nickel foil (thickness 0.05 mm) with diameters of effusion orifice (0.2486±0.0004) mm at $T > 273$ K and (0.5607±0.0004) mm at $T < 273$ K for crystal 1-MeCPol and (0.2483±0.0004) mm for liquid 1,1-ClMeCP were used. The solution of water and ethanol (50 : 50 mass) and crystaline CO_2 were taken as a thermostating liquid and a quenching agent, respectively, in the experiments at $T < 273$ K. It was supposed for calculations that vapors have a monomolecular composition. The uncertainty in vapor pressures determination does not exceed ±5%. The apparatus construction and measuring procedure were described in details earlier [5,6].

The combustion enthalpy for 1-MeCHol was determined by burning in a bomb calorimeter with an isothermal water shell, the temperature of which remained constant within ±0.0015 K. The measurements uncertainty for combustion energies is 0.02% [7]. The reliability of determination of the combustion enthalpies is indirectly confirmed by a good agreement of our value of the combustion enthalpy of urea with the results obtained by other authors [8]. Thermometric measurements were carried out by the 100 Ω platinum resistance thermometer with recording of amplified signal of a digital voltmeter. Energy equivalent of calorimeter (14932.4±5.7) J K^{-1} was determined from reference sample of benzoic acid (K-1) with combustion energy (−26434.6±4.5) J g^{-1} (at weighting in vacuum). The samples of 1-MeCPol were burnt in hermetically sealed Terylene ampoules (Terylene is polyethylene terephthalate with $d_4^{20} = 1380\,\mathrm{kg\,m^{-3}}$, C_p (298.15 K)=1.142 J K^{-1} g^{-1} [9]). Combustion energy of Terylene is (22879.7± 11.1) J g^{-1} (at weighting in vacuum). The completeness of burning was checked by gravimetric analysis of combustion products using the Rossini method [10]. The Washburn corrections were calculated by the Prosen method and recommendations [11].

The IR spectra of liquid 1-MeCPol and 1,1-ClMeCP in the wave-number range from 75 to 450 cm^{-1} were recorded using a Fourier spectrometer LAFS 1 000 with resolution of 2.9 cm^{-1}. The spectra were obtained from interferograms, averaged over five experiments. The IR spectra in the range from 4 000 to 400 cm^{-1} were recorded with a Specord-75 IR spectrometer using thin films of liquids between KBr plates. The Raman spectra between 4 000 and 400 cm^{-1} were obtained by a Ramalog-4 spectrometer with argon laser ($\lambda_B = 414.5$ nm).

3. Thermodynamic properties and characteristics of phase transitions of 1-MeCPol and 1,1-ClMeCP

It was reported earlier [3] that 1-MeCPol undergoes the transition crIII → crII at 281.72 K. That is why it is necessary to note that the limitations of the Knudsen method in determining saturated vapor pressures of compounds (approximately from 0.03 to 300 Pa) allow to obtain the reliable data only over the phase crIII of 1-MeCPol. But the enthalpy of sublimation determined in MID-200 is related to phase crII. Taking into account the changes of both temperature and solid phase of 1-MeCPol at 281.72 K, the calorimetric enthalpy of sublimation was reduced

Table 1
Saturated vapor pressures P over crystal (crIII) 1-MeCPol and liquid 1,1-ClMeCP measured by the integral effusion Knudsen method: τ is the duration of effusion; Δm is sample mass decrease

Compounds	T (K)	τ (s)	$\Delta m \times 10^6$ (kg)	P (Pa)
1-MeCPol	253.11	7254	9.92	2.192
	258.12	5454	14.73	4.371
	260.58	3654	13.40	5.965
	263.05	2454	12.51	8.339
	265.39	1854	12.40	10.98
	273.12	5454	16.69	28.58
	276.04	2754	11.79	40.20
	278.83	2154	12.69	55.60
	281.58	1854	14.84	75.91
1,1-ClMeCP	239.34	2754	17.10	50.01
	244.49	1854	18.25	80.13
	247.16	1869	23.61	103.41
	253.02	1854	36.80	164.38
	253.16	1854	37.37	167.01
	258.15	1854	54.83	247.44
	263.28	1854	78.96	359.82

to a comparison between the results of two different methods.

The measured saturated vapor pressures over crystalline 1-MeCPol (crIII) between 253 and 281 K and over liquid 1,1-ClMeCP between 239 and 263 K are presented in Table 1. The experimental results for 1-MeCPol (crIII) and for 1,1-ClMeCP can be approximated by Eqs. (1) and (2), respectively:

$$\ln(P/\mathrm{Pa}) = (35.800 \pm 0.160) - (8862.0 \pm 42.9)/T \qquad (1)$$

$$\ln(P/\mathrm{Pa}) = (25.600 \pm 0.478) - (5186.6 \pm 120.0)/T \qquad (2)$$

The enthalpy of sublimation of 1-MeCPol $\Delta^g_{\mathrm{crIII}}H^0_m(267.35\,\mathrm{K}) = (73.68 \pm 0.36)\,\mathrm{kJ\,mol^{-1}}$ and the enthalpy of vaporization of 1,1-ClMeCP $\Delta^g_{\mathrm{l}}H^0_m(251.31\,\mathrm{K}) = (43.12 \pm 0.99)\,\mathrm{kJ\,mol^{-1}}$ at the mean temperatures of their effusion experiments were calculated from Eqs. (1) and (2), respectively. The values $\Delta^g_{\mathrm{crII}}H^0_m(290.52\,\mathrm{K}) = (67.35 \pm 0.17)\,\mathrm{kJ\,mol^{-1}}$ for 1-MeCPol and $\Delta^g_{\mathrm{l}}H^0_m(296.60\,\mathrm{K}) = (39.74 \pm 0.12)\,\mathrm{kJ\,mol^{-1}}$ for 1,1-ClMeCP were also determined from calorimetric experiments (Tables 2 and 3, respectively). The weight-averaged enthalpies of evaporation, obtained from calorimetric and effusion results, were used in the further calculations and they are $\Delta^g_{\mathrm{crIII}}H^0_m(267.35\,\mathrm{K}) = (71.78 \pm 0.15)\,\mathrm{kJ\,mol^{-1}}$ for 1-MeCPol and $\Delta^g_{\mathrm{l}}H^0_m(251.31\,\mathrm{K}) = (42.07 \pm 0.12)\,\mathrm{kJ\,mol^{-1}}$ for 1,1-ClMeCP. Then, taking into account the effusion data, the standard entropies of sublimation of 1-MeCPol and of vaporization of 1,1-ClMeCP are, respectively: $\Delta^g_{\mathrm{crIII}}S^0_m(267.35\,\mathrm{K}) = (194.70 \pm 0.56)\,\mathrm{J\,K^{-1}\,mol^{-1}}$ and $\Delta^g_{\mathrm{l}}S^0_m(251.31\,\mathrm{K}) = (112.82 \pm 0.48)\,\mathrm{J\,K^{-1}\,mol^{-1}}$. On the basis of these values and entropies of compounds in the condensed state [3], the experimental entropies of gaseous 1-MeCPol and 1,1-ClMeCP were calculated and they are, respectively:

$$S^0_m(g; 267.35\,\mathrm{K}) = (354.49 \pm 0.90)\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

and

$$S^0_m(g; 251.31\,\mathrm{K}) = (338.77 \pm 1.23)\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

The results of combustion experiments for 1-MeCPol are summarized in Table 4. The standard molar energy and enthalpy of combustion of crystal 1-MeCPol are, respectively:

$$\Delta_c U^0_m(\mathrm{crII}; 298.15\,\mathrm{K}) = -(3718.60 \pm 1.14)\,\mathrm{kJ\,mol^{-1}};$$

$$\Delta_c H^0_m(\mathrm{crII}; 298.15\,\mathrm{K}) = -(3724.80 \pm 1.14)\,\mathrm{kJ\,mol^{-1}}.$$

Table 2
Calorimetric determinations of the enthalpy of sublimation for 1-MeCPol

No.	m (g)	T (K)	$\int_{\tau=0}^{\tau_2} \Delta E \cdot d\tau$ (mV s)	Type of cell	ΔH (J)	$\Delta_{\text{crII}}^{g} H_m^0$ (kJ mol^{-1})
1	0.12192	291.69	18545.69	A	81.90	67.28
2	0.12192	289.64	19169.57	A	84.65	67.47
3	0.10734	290.03	16283.33	A	71.91	67.10
4	0.09557	291.71	13861.62	B	64.48	67.57
5	0.11710	289.91	16929.28	B	78.74	67.35
6	0.11906	290.19	17206.13	B	80.03	67.33
		$\langle \Delta_{\text{crII}}^{g} H_m^0 (290.52\,\text{K}) \rangle = (67.35 \pm 0.17)\,\text{kJ}\,\text{mol}^{-1}$				

The calorimetrically measured enthalpy change ΔH and the enthalpy ΔH_m^0 were calculated from the expressions:

$$\Delta H = K^{-1} \cdot \int_{\tau=0}^{\tau_2} \Delta E \cdot d\tau \quad \text{and} \quad \Delta H_m^0 = \Delta H \cdot M/m,$$

where m is the mass of the specimen; M is the molar mass; K is the calorimetric constant (the K values for cells A and B are 226.45 and 214.99 mV s J^{-1}, respectively); ΔE is the thermocouple potential difference corresponding to the temperature imbalance between cell and calorimeter thermostat at the time τ; τ_2 is the experiment duration; T is the temperature of the calorimeter. The value of m is corrected for the mass of saturated vapor in the free volume of the ampoule immediately before an experiment.

Table 3
Calorimetric determinations of the enthalpy of vaporization for 1,1-ClMeCP

No.	m (g)	T (K)	$\int_{\tau=0}^{\tau_2} \Delta E \cdot d\tau$ (mV s)	Type of cell	ΔH (J)	$\Delta_{l}^{g} H_m^0$ (kJ mol^{-1})
1	0.08039	296.10	6130.51	A	26.95	39.77
2	0.08449	396.92	6433.09	A	28.41	39.88
3	0.06591	297.01	5022.80	A	22.18	39.91
4	0.08172	296.14	5866.66	B	27.29	39.61
5	0.07667	295.87	5509.79	B	25.63	39.65
6	0.07537	297.09	5418.72	B	25.20	39.66
7	0.06400	297.08	4601.99	B	21.41	39.67
		$\langle \Delta_{l}^{g} H_m^0 (296.60\,\text{K}) \rangle = (39.74 \pm 0.12)\,\text{kJ}\,\text{mol}^{-1}$				

See footnote of Table 2.

On the basis of the standard enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ [12] and the weight-averaged enthalpy of sublimation $\Delta_{\text{crIII}}^{g} H_m^0(298.15\,\text{K}) = (66.99 \pm 0.15)\,\text{kJ}\,\text{mol}^{-1}$, the standard molar enthalpies of formation of crystal and gaseous 1-MeCPol were obtained:

$$\Delta_f H_m^0(\text{crII}; 298.15\,\text{K}) = -(351.26 \pm 1.40)\,\text{kJ}\,\text{mol}^{-1};$$

$$\Delta_f H_m^0(g; 298.15\,\text{K}) = -(284.15\,\text{K}) = -(284.27 \pm 1.41)\,\text{kJ}\,\text{mol}^{-1}.$$

4. Conformational compositions, normal vibrational frequencies and statistical calculations of thermodynamic functions of 1-MeCPol and 1,1-ClMeCP in the ideal gas state

To analyze the conformational compositions of gaseous 1-MeCPol and 1,1-ClMeCP and to obtain geometrical parameters and energy characteristics of internal rotation and ring inversion of molecules, the molecular mechanics methods [13] were used by the MM2 program.

Table 4
Experimental determinations of the molar energy of combustion of crystal 1-MeCPol (crII) at 298.15 K, where m is the mass of the substance; δ is the correction for the heat exchange between the calorimeter vessel and surroundings; K is the cooling constant of the calorimeter; ΔT is the corrected temperature rise; q_i is the correction for ignition; q_{HNO_3} is the correction for nitric acid formation; q_{wash} is the sum of the Washburn corrections; m_{teryl} is the mass of Terylene; q_{teryl} is the energy of combustion of Terylene

No.	1	2	3	4	5
m (g)	0.48019	0.42288	0.39451	0.40503	0.51121
m_{teryl} (g)	0.02516	0.02876	0.02467	0.02872	0.02824
$K\times10^{-3}$	1.156	1.202	1.176	1.140	1.187
$-\delta$ (K)	0.017	0.021	0.019	0.015	0.013
ΔT (K)	1.23380	1.09610	1.01954	1.05173	1.31563
q_i (J)	2	2	2	2	2
q_{HNO_3} (J)	6.3	5.1	5.4	6.3	6.3
q_{wash} (J)	7.0	6.1	5.6	5.8	7.6
q_{teryl} (J)	575.6	658.0	564.4	657.1	646.1
$-\Delta_c U_m^0$ (J g^{-1})	37136.7	37117.5	37126.6	37117.3	37134.6
		Average value: (37126.5±11.4) J g^{-1}			

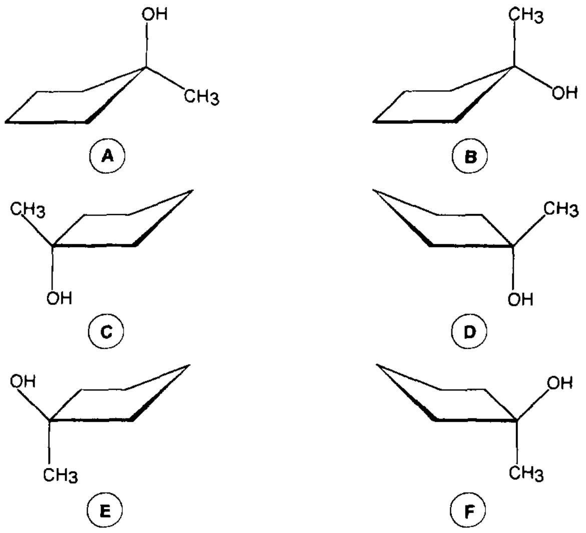

Fig. 1. The conformers of 1-MeCPol.

It was found that six and two conformers of the 'envelope' form are stable for 1-MeCPol (Fig. 1) and for 1,1-ClMeCP, respectively. The conformers of 1,1-ClMeCP (A and B) are structurally similar with the conformers A and B of 1-MeCPol. Besides, four conformers of 1-MeCPol form two pairs of chiral isomers (pairs C and D, E and F). The most stable conformers of compounds are conformers A with pseudo-equatorial methyl group. Principal moments of inertia products, reduced moments of inertia of tops and energy differences for conformers of 1-MeCPol and 1,1-ClMeCP at 298.15 K are given in Table 5.

The energetics of conformational transitions and tops rotations in molecules of 1-MeCPol and 1,1-ClMeCP were investigated by the 'dihedral driver' procedure of the MM2 program. This procedure allows to study the alteration of molecular energy at various molecular dihedral angles. The pseudorotation was examined at the fixed positions of OH- and CH_3-tops and the configuration of carbon ring was the same at rotations of methyl and hydroxyl groups because the potential barriers of conformational conversions and internal rotations differ significantly. The energy changes at pseudorotation in 1,1-ClMeCP and rotations of the tops in molecules of 1-MeCPol and 1,1-ClMeCP were approximated by the potential-energy functions of general type:

$$V(\phi) = V_0/2 + \sum_{i=1}^{n} V_n \cdot \cos(n\phi) \qquad (3)$$

where V_0 and V_n are coefficients given in Table 6, n is the number of maximums in the potential curve, ϕ is the angle of rotation of the top or a phase angle of pseudorotation. The potential-energy function of pseudorotation in 1,1-ClMeCP is also represented in Fig. 2.

To carry out the vibrational assignments for 1-MeCPol and 1,1-ClMeCP, the normal vibrational forms and wave numbers of their conformers A were

Table 5
Principal moments of inertia products ($I_AI_BI_C$), reduced moments of inertia of the tops (I_{red}) and energy differences at 298.15 K ($\Delta_{conf}H^0_m$) for conformers of 1-MeCPol and 1,1-ClMeCP.

Compounds	Types conformer	$I_AI_BI_C$ 10^{114} g^3 cm^6	$I_{red}(CH_3)$ 10^{40} g cm^2	I_{red}(OH) 10^{40} g cm^2	$\Delta_{conf}H^0_m$ kJ mol^{-1}
1-MeCPol	A	30.68	5.30	1.29	0
	B	31.67	5.33	1.29	3.79
	C,D	32.03	5.31	1.29	0.44
	E,F	31.97	5.31	1.29	0.52
1,1-ClMeCP	A	65.43	5.33	—	0
	B	71.02	5.33	—	6.13

Table 6
The coefficients of the potential-energy functions of the internal rotation for 1-MeCPol and 1,1-ClMeCP

Compounds	Types of internal rotation	$V_0/2$ (J mol^{-1})	V_1 (J mol^{-1})	V_2 (J mol^{-1})	V_3 (J mol^{-1})
1-MeCPol	CH_3-top rotation	7210	—	—	7210
	OH-top rotation	1740	−285	−80	1625
1,1-ClMeCP	CH_3-top rotation	8930	—	—	8930
	pseudorotation	5800	−3060	−2740	—

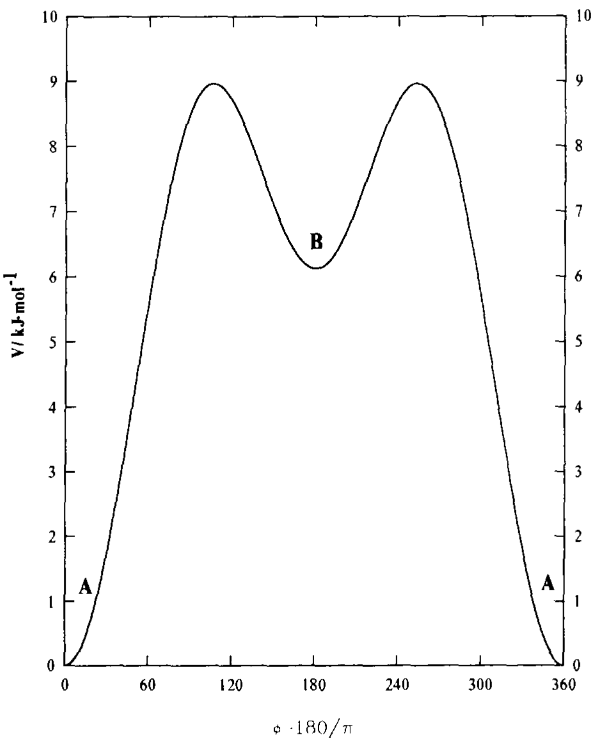

Fig. 2. The potential-energy function of pseudorotation for 1,1-ClMeCP: ϕ is a phase angle of pseudorotation, A and B denote the conformers of 1,1-ClMeCP.

calculated by the programs, given in Ref. [14]. The torsional coordinate of methyl group was not taken into consideration for these calculations. Geometrical parameters of molecules were obtained by the MM2 program. The force-field constants of cyclopentyl skeleton and methyl group were the same as for methylcyclopentane [15]. Other force-field constants of 1-MeCPol and 1,1-ClMeCP were the same as for 1-methylcyclohexanol and 1-chloro-1-methylcyclohexane [16], respectively. The results of vibrational analyses of 1-MeCPol and 1,1-ClMeCP are presented in Tables 7 and 8.

Statistical calculations of thermodynamic properties of 1-MeCPol and 1,1-ClMeCP in the ideal gas state were made using the procedures and relations given in [17]. The method of determining conformational contributions was chosen to reach the best possible agreement between experimental and calculated entropies of gaseous compounds.

Vibrational contributions to thermodynamic functions of 1-MeCPol and 1,1-ClMeCP were obtained from wave numbers selected for statistical calculations (see Tables 7 and 8). The bands 380 cm^{-1} of 1-MeCPol and 125 cm^{-1} of 1,1-ClMeCP corresponding to rotational vibration of the hydroxyl group and pseudorotation, respectively, were ignored. Contributions of hindered rotations of methyl and hydroxyl

Table 7
Observed ($\bar{\nu}_0$) and calculated ($\bar{\nu}_c$) wavenumbers and potential energy distribution (P.E.D. (%)) for 1-MeCPol.

No.	$\bar{\nu}_c$(cm^{-1})	$\bar{\nu}_0$(cm^{-1})		P.E.D. (%)	$\bar{\nu}_0$(cm^{-1}) selected for statistical calculations
		IR	Raman		
1	3681	3350		OH (100)	3350
2	2983	2960	2965	CHm (99)	2965
3	2979			CHm (100)	2965
4	2951	2920	2930	CH (98)	2930
5	2948			CH (99)	2930
6	2941			CH (99)	2930
7	2937			CH (99)	2930
8	2881	2870	2880	CH (99)	2880
9	2877			CH (99)	2880
10	2877			CH (99)	2880
11	2876			CH (99)	2880
12	2870	2850	2860	CHm (100)	2860
13	1476	1480		CCH (24); HCH (75)	1480
14	1472	1470		CCH (22); HCH (77)	1470
15	1469	1460		CCH (23); HCH (76)	1460
16	1465	1455	1455	CCH (22); HCH (77)	1455
17	1435	1445		CCHm (15); HCHm (84)	1445
18	1411	1410		CCHm (5); HCHm (94)	1410
19	1390		1395	CC (22); CCm (6); CCH (51)	1395
20	1368	1370		CC (11); CCH (85)	1370
21	1355	1360		CCHm (51); HCHM (41)	1355
22	1340	1310		CC (36); CCH (47)	1310
23	1329	1300		CC (30); CCH (65)	1300
24	1286	1285	1290	CC (7); CO (17); CCH (33) CCHm (6); COH (18)	1290
25	1225	1255	1240	CC (38); CCH (24); CCHm (17)	1240
26	1224	1230	1220	CCm (14); CO (11); CCH (34); COH (27)	1220
27	1163	1150		CCH (98)	1150
28	1161			CC (6); CCH (85)	1150
29	1124	1125	1130	CCH (96)	1125
30	1082			CC (11); CCm (19); CCH (12) CCHm (8); COH (34)	1125
31	1077			CCm (18); CO (8); CCH (57)	1125
32	1045	1035	1040	CCH (85); CCHm (5)	1035
33	1032	1020		CC (57); CCH (33)	1020
34	983	1005		CCC (7); CCH (32); CCHm (56)	1005
35	946	975	985	CCH (32); CCHm (53); HCHm (5)	985
36	922	930	940	CC (54); CCH (10); CCHm (23)	940
37	905	900	915	CC (74); CCC (5); CCH (11)	915
38	867	880	890	CC (9); CO (37); CCH (35); CCHm (9)	890
39	809	815	825	CC (7); CCH (89)	825
40	788		810	CC (24); CO (6); CCC (12); CCH (49)	810
41	730	720		CC (19); CO (23); CCH (48)	720
42	595	585	595	CCC (79); CCH (13); CCO (5)	595
43	528	515		CCm (19); CCC (43); CCCm (10); CCH (5); CmCO (7)	515
44	445		480	CCO (56); tCO (43)	480
45	419	420		CCC (29); CCCm (11); CCH (15) CCO (22); t–r (14)	420

Table 7
(Continued)

No.	$\bar{\nu}_c$(cm^{-1})	$\bar{\nu}_0$(cm^{-1})		P.E.D. (%)	$\bar{\nu}_0$(cm^{-1}) selected for statistical calculations
		IR	Raman		
46	375	375	380	CCCm (28); tCO (71)	—
47	326	310	320	CCCm (17); CCO (7); CmCO (73)	320
48	314	310	320	CCCm (64); CCO (20); t–r (7)	320
49	222	225	200	CCC 95); CCO 97); t–r (86)	225
50	150	175		CCC (24); CCCm (18); CCO (9); t–r (45)	175

In columns 3 and 4 values of ($\bar{\nu}_0$) are given for the vibrations assigned from IR and Raman spectra. The numbers of normal vibrations of 1-methylcyclopentanol are in parentheses. Torsinal coordinate of methyl group was not taken into consideration at wavenumbers calculations

Table 8
Observed ($\bar{\nu}_0$) and calculated ($\bar{\nu}_c$) wave numbers and potential energy distribution (P.E.D. (%)) for 1,1-ClMeCP

No.	$\bar{\nu}_c$(cm^{-1})	$\bar{\nu}_0$(cm^{-1})		P.E.D. (%)	$\bar{\nu}_0$(cm^{-1}) selected for statistical calculations
		IR	Raman		
1	2983	2965	2970	CHm (99)	2970
2	2979			CHm (99)	2970
3	2951	2930	2930	CH (98)	2930
4	2948			CH (99)	2930
5	2941	2900	2920	CH (99)	2900
6	2938			CH (99)	2900
7	2881	2865	2880	CH (99)	2880
8	2877			CH (99)	2880
9	2877			CH (99)	2880
10	2876	2850		CH (99)	2880
11	2870			CHm (100)	2880
12	1475	1460	1450	CCH (23); HCH (73)	1450
13	1472			CCH (22); HCH (77)	1450
14	1469			CCH (24); HCH (70)	1450
15	1465	1440		CCH (21); HCH (78)	1450
16	1460			CCL (10); CCH (14); CCHm (13); HCH (17); HCHm (25)	1450
17	1411	1375		CCl (10); CCH (9); HCHm (67)	1375
18	1410			CCHm (5); HCHm (94)	1375
19	1368			CC (11); CCC (12); CCH (85)	1375
20	1367			CCH (49); CCHm (17); HCHm (14)	1375
21	1348	1330	1330	CC (17); CCH (38); CCHm (25)	1330
22	1327	1305		CC (28); CCH (67)	1305
23	1321	1285		CC (31); CCH (45); CCHm (9)	1285
24	1207	1225	1200	CC (33); CCH (33); CCHm (16)	1200
25	1165	1190		CCC (12); CCH (98)	1190
26	1156	1165	1150	CC (11); CCH (75); CCHm (7)	1150
27	1121	1130		CCC (10); CCH (88)	1130
28	1105	1100		CCH (90)	1100
29	1058	1035		CC (17); CCm (43); CCC (7) CCHm (12); CmCl (7)	1035
30	1041			CCC (6); CCH (86)	1035
31	1026	1020		CC (55); CCC (5); CCH (31)	1020
32	982	980		CC (39); CCH (20); CCHm (31)	980
33	943	930		CC (15); CCH (26); CCHm (44)	930

Table 8
(Continued)

No.	$\bar{\nu}_c$(cm^{-1})	$\bar{\nu}_0$(cm^{-1})		P.E.D. (%)	$\bar{\nu}_0$(cm^{-1}) selected for statistical calculations
		IR	Raman		
34	917	910		CC (54); CCCH (10); CCHm (23)	910
35	907	885	890	CC (44); CCH (25); CCHm (15)	885
36	894	845	860	CC (49); CCm (5); CCH (36)	845
37	809	835		CC (6); CCC (6); CCH (90)	835
38	774	775	785	CCC (12); CCH (86)	775
39	602	590	590	CC (20); CCl (31); CCC (16) CCC (16); CCH (19)	590
40	583			CCC (49); CCH (13); CCCl (5)	590
41	540	535	550	CCm (25); CCC (35); CCCm (10); CCCl (7); CmCl (5)	535
42	374	370	370	CCCm (50); CCCl (38)	370
43	367			CCl (35); CCC (11); CCCm (8); CCCl (13); CmCl (9); t–r (9)	370
44	325	305		CCCm (17); CCCl (15); CmCl (57)	305
45	288			CCCm (25); CCCl (47); t–r (20)	305
46	201	180		CCC (6); CCCl (41); t–r (45)	180
47	135	125		CCC (19); CCCm (10); CCCl (11); t–r (56)	125

In columns 3 and 4 values of $\bar{\nu}_0$ are given for the vibrations assigned from IR and Raman spectra. The numbers of normal vibrations of 1-chloro-1-methylcyclopentane are in parentheses. Torsinal coordinate of methyl group was not taken into considerations at wavenumbers calculations.

tops were determined from energy levels, calculated using the Shroedinger's equation for the aforementioned potential functions (Table 6).

Conformational contributions to thermodynamic properties of gaseous 1-MeCPol were obtained as contributions of vibration 200 cm^{-1}, corresponding to pseudorotation (Table 7), while taking into account the corrections on mixing of conformers. The calculated entropy of 1-MeCPol in the gaseous state $S^0_m(\mathrm{g}; 267.35\,\mathrm{K}) = 355.82\,\mathrm{J\,K^{-1}\,mol^{-1}}$ is in a good agreement with the experimental value $S^0_m(\mathrm{g}; 267.35\,\mathrm{K}) = (354.48 \pm 0.90)\,\mathrm{J\,K^{-1}\,mol^{-1}}$ (the divergence is about 0.4%).

Contributions of pseudorotation to thermodynamic functions of 1,1-ClMeCP were determined from energy levels calculated for the foregoing potential function (Table 6). In order that there may be an agreement between the experimental and calculated

Table 9
Standard molar thermodynamic functions of 1-methylcyclopentanol in the ideal gas state ($p^0 = 101325\,\mathrm{Pa}$)

T (K)	$\Delta_0^T S^0_m$ (J K^{-1} mol^{-1})	$C_{p,m}$ (J K^{-1} mol^{-1})	$\Delta_0^T H^0_m/T$ (J K^{-1} mol^{-1})	Φ^0_m (J K^{-1} mol^{-1})
100	275.41	57.10	44.97	230.44
200	325.66	91.75	59.71	265.95
298.15	369.36	130.89	76.52	292.85
300	370.18	131.68	76.86	293.32
400	413.89	173.87	95.88	318.00
500	456.83	211.39	115.33	341.50
600	498.24	242.81	134.04	364.19
700	537.69	269.00	151.51	386.19
800	575.09	291.06	167.61	407.48
900	610.49	309.85	182.40	428.09
1000	643.99	325.92	195.97	448.02

Table 10
Standard molar thermodynamic functions of 1,1-ClMeCP in the ideal gas state ($p^0 = 101325\,\mathrm{Pa}$)

T (K)	$\Delta_0^T S_m^0$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$C_{p,m}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$\Delta_0^T H_m^0/T$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	Φ_m^0 ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
100	263.81	56.94	42.58	221.23
200	314.90	94.99	59.24	255.66
298.15	359.94	133.48	77.30	282.65
300	360.77	134.22	77.64	283.13
400	404.79	173.16	96.71	308.07
500	447.22	207.55	115.54	331.69
600	487.69	236.33	133.34	354.35
700	525.97	260.29	149.82	376.16
800	562.08	280.42	164.92	397.16
900	596.12	297.47	178.73	417.40
1000	628.24	312.00	191.35	436.89

entropies of gaseous 1,1-ClMeCP at 251.31 K, the pseudorational moment of inertia $15.24\times10^{-40}\,\mathrm{g\,cm^2}$ was accepted. This value is in good accord with the pseudorotational moments of inertia adopted for cyclopentanol ($15.3\times10^{-40}\,\mathrm{g\,cm^2}$ [1]) and chlorocyclopentane ($19.3\times10^{-40}\,\mathrm{g\,cm^2}$ [2]). Thermodynamic properties of 1-MeCPol and 1,1-ClMeCP in the ideal gas state between 100 and 1 000 K are given in Tables 9 and 10, respectively.

5. Molecular rotation in the plastic crystal state of 1,1-ClMeCP

As it was reported in our recent paper [3], 1,1-ClMeCP forms plastic crystals between 178.82 and 189.05 K. According to conventional knowledge [18,19], the transition of organic compounds into the plastic crystal state can be caused by the removal of prohibitions of internal rotation in molecules and a general rotation of molecules in nodes of crystal lattice. Contributions of ring inversion and methyl tops rotation to the entropy of 1,1-ClMeCP (the ideal gas state, isolated molecules) at 178.82 K were calculated by the statistical thermodynamics methods, and these are, respectively: 3.82 and $15.82\,\mathrm{J\,K^{-1}\,mol^{-1}}$. Hence, it is necessary to admit a possibility of general rotation of 1,1-ClMeCP molecules in the plastic crystal state because the sum of these two contributions is essentially lower than the entropy of solid-to-solid transition $\Delta_{\mathrm{crII}}^{\mathrm{crI}} S_m^0(178.82\,\mathrm{K}) = 31.89\,\mathrm{J\,K^{-1}\,mol^{-1}}$ [3]. This molecular rotation should be very hindered because the contribution of free rotation of molecules to entropy at 178.82 K is $S_{\mathrm{rot}} = 110.64\,\mathrm{J\,K^{-1}\,mol^{-1}}$ and this contribution significantly exceeds the value $\Delta_{\mathrm{crII}}^{\mathrm{crI}} S_m^0$ for 1,1-ClMeCP.

Acknowledgements

The authors express their thanks to the Foundation of the Fundamental Research of the Republic of Belarus (Grant MP-34) and the International Science Foundation (Grant MW 4300) for sponsoring this work.

G.J. Kabo, A.A. Kozyro and A.V. Blokhin are grateful to the International Soros Science Education Program for financial support in carrying out of the present work.

References

[1] G.J. Kabo, V.V. Diky, A.A. Kozyro, A.P. Krasulin and V.M. Sevruk, J. Chem. Thermodynamics, 27 (1995) 953.
[2] V.V. Diky, G.J. Kabo, A.A. Kozyro, A.P. Krasulin and V.M. Sevruk, J. Chem. Thermodynamics, 25 (1993) 1169.
[3] G.J. Kabo, A.V. Blokhin, A.A. Kozyro and V.V. Diky, Thermochimica Acta, 290 (1996) 13.
[4] V.M. Sevruk, V.V. Simirsky, G.J. Kabo, A.A. Kozyro and A.P. Krasulin, Zh. Fiz. Khim., 64 (1990) 3402.
[5] A.P. Krasulin, A.A. Kozyro and G.J. Kabo, Zh. Prykl. Khim., 60 (1987) 104.
[6] A.P. Krasulin, A.A. Kozyro, Vestnic Beloruss. Gos. Universiteta, Ser. 2, 3 (1987) 20.

[7] M.L. Frenkel, G.V. Kaler, V.V. Simirsky and G.J. Kabo, Zh. Fiz. Khim, 63 (1989) 2277.

[8] H.P. Diogo and M.E. Minas da Piedade, J. Chem. Thermodynamics, 27 (1995) 197.

[9] C.W. Smitha and M. Dole, J. Polimer Sci., 20 (1956) 37.

[10] F.D. Rossini (Ed.), Experimental Thermochemistry, Interscience, New York – London, 1956, v.1, Chapter 4.

[11] Yu. I. Aleksandrov, B.N. Oleynic, T.R. Usvyateva, Trudy Metrolog. Inst. SSSR, Izd. Standartov, Moscow, Leningrad, (1971) 155, 189.

[12] V.A. Medvedev and I.L. Kodakovsky, Uspekhi Khimii, 48 (1979) 2164.

[13] U. Burkert, N. Allinger, Molecular Mechanics, Am. Chem. Soc., Washington, D.C., 1982.

[14] L.A. Gribov, V.A. Dement'ev, Methods and Algorithms of Calculations in Theory of Vibrational Spectra of Molecules, Nauka, Moskow, 1981.

[15] M.J. Alyamberg, Yu. Z. Karasev, V.V. Dement'ev, L.A. Gribov, Interpretirovannye Kolebatelnye Spectry Uglevodorodov -Proizvodnykh Tcyclogeksana i Tcyclopentana, Nauka, Moscow, 1988.

[16] G.J. Kabo, A.V. Blokhin, A.A. Kozyro, V.V. Diky, A.P. Krasulin, L.S. Ivashkevitch, M.L. Frenkel, V.M. Sevruk, Yu. V. Maksimuk, J. Chem. Thermodynamics, (1996), to be published.

[17] M.L. Frenkel, G.J. Kabo, K.N. Marsh, G.N. Roganov, R.C. Wilhoit, Thermodynamics of Organic Compounds in the Gas State, Thermodynamics Research Center, Texas USA, 1994.

[18] J.J. Timmermans, Phys. Chem. Solids, 18 (1961) 1.

[19] D. Fox, M.M. Labes, A. Weissberger (Eds.), Physics and Chemistry of the Organic Solid State, Interscience, New York - London, 1965.