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Thermodynamics of 2-(1′-Hydroxycyclohexyl)cyclohexanone: Vaporization, Sublimation, and the Ideal Gas State Thermodynamic Properties

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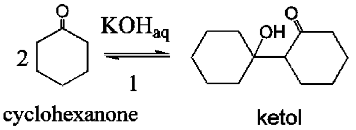
The thermodynamics of one of the byproducts of caprolactam production, 2-(1′-hydroxycyclohexyl)cyclohexanone (ketol), have been studied in this work. Saturated vapor pressure for liquid and crystalline ketol was measured by the Knudsen method in the temperature ranges from (308.2 to 330.4) K and from (289.6 to 300.8) K, respectively. Additionally, the saturated vapor pressures over ketol in the undercooled state and in the liquid were measured by the transpiration method in the temperature range from (287.9 to 303.0) K and from (308.0 to 351.5) K, respectively. The enthalpy of vaporization and the enthalpy of sublimation of ketol at the average temperatures studied were obtained indirectly from the temperature dependence of the vapor pressure measured by the Knudsen method as well as by the transpiration method. Furthermore, the standard molar enthalpy of sublimation was measured directly at 303.1 K using calorimetry. The entropy of ketol in the vapor state at (320.8 and 298.2) K was derived. The thermodynamic properties for 2-(1′-hydroxycyclohexyl)cyclohexanone in the ideal gas state were calculated from statistical mechanic calculations in the broad temperature range from (50 to 1000) K. The gaseous thermodynamic equilibrium constant $K°$ (at 332.1 K) for cyclohexanone auto-condensation (side reaction of the caprolactam production) leading to 2-(1′-hydroxycyclohexyl)cyclohexanone was assessed.

Introduction

Auto-condensation of cyclohexanone leading to the formation of 2-(1′-hydroxycyclohexyl)cyclohexanone (ketol) according to reaction I[1]



(I)

is one of the first side reactions at the initial stage of caprolactam production. Furthermore, auto-condensation of ketones is an important reaction for the synthesis of bicyclic ketones, alcohols, and phenylphenols. Thermodynamic properties of ketol in the condensed state and equilibrium study of reaction involving this compound have been reported recently.[2] In this paper, results derived from vapor pressure measurements of the ketol together with the direct calorimetric determination of the vaporization enthalpy of the ketol as well as calculation of the thermodynamic properties of the ketol in the ideal gas state are reported.

Experimental Section

Sample. The sample of 2-(1′-hydroxycyclohexyl)cyclohexanone was prepared by cyclohexanone dimerization with a water solution of KOH as catalyst according to the procedure described in ref 1. The compound was purified by re-crystallization from petroleum ether and finally distilled at $T = (313 \text{ to } 318)$ K and $p = 0.3$ kPa. The mole fraction purity of the ketol used in experiments was 0.9982 according to the fractional melting analysis.[2]

Vapor Pressure Measurements, Knudsen Method. The procedure of measurements has been described in detail.[3] Uncertainty in vapor pressure was estimated to be 5 %. The improved Knudsen cell with enlarged contact surface was used[4] for the measurements of the solid sample. Two membranes with the following parameters were used for the measurements: the first one with thickness $l = (50 \pm 2)\cdot 10^{-3}$ mm and the average effusion orifice diameter $d = (0.8370 \pm 0.0005)$ mm, and the second one with $l = (84 \pm 2)\cdot 10^{-3}$ mm and $d = (0.4467 \pm 0.0005)$ mm. Mass loss in each experiment was from (4 to 12) mg. The vapor pressures were calculated using the following equation[3]:

$$p_{\text{sat}} = p^* + \frac{1}{\alpha}\left(k\frac{S_{\text{orif}}}{S_{\text{samp}}}p^*\right) \tag{1}$$

where p_{sat} is the equilibrium vapor pressure of the substance; S_{samp} is the geometric surface of the sample; S_{orif} is the area of the effusion orifice; k is the transmission probability coefficient through the effusion orifice; α is the condensation coefficient; p^* is the vapor pressure in the cell calculated as

$$p^* = \frac{\Delta m}{kS_{\text{orif}}\tau}\sqrt{\frac{2\pi RT}{M}} \tag{2}$$

Δm is the mass loss of the sample during the exposure time τ; T is the temperature of the heat carrier in the thermostat; and M is the molar mass of the substance (assumption that the vapor of ketol tends to be monomolecular has been made according

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to arguments given in the discussion below). The k coefficient was determined according to Wahlbeck's theory[3] as described in refs 4 and 5. An effective diameter of ketol molecule $\sigma = 7.214 \cdot 10^{-10}$ m was calculated from a van der Waals volume assuming the molecule to be spherical. The van der Waals volume was estimated by the geometric parameters of ketol obtained from quantum-mechanical calculations and the known atomic radii.[6] The condensation coefficient $\alpha = 5 \cdot 10^{-3}$ for the crystalline state was determined from eq 1 taking into account that in the triple point $T_{tr} = 306.75$ K,[2] $p_{sat,liq}(T_{tr}) = p_{sat,cr}(T_{tr})$ and $\alpha = 1$ for the liquid state.

Vapor Pressure Measurements, Transpiration Method. Vapor pressure of the liquid ketol and its enthalpy of vaporization were also determined by the transpiration method.[7,8] A sample of approximately 0.5 g was mixed with glass beads (diameter of a bead was 1 mm) and placed in thermostated U-tube of length 20 cm and diameter 0.5 cm. Preheated nitrogen stream with flow from (2 to 6) $\mathrm{dm^3 \cdot h^{-1}}$ was passed through the U-tube at constant temperature (± 0.1 K), and the transported amount of material was condensed in a cooled trap ($T = 243$ K). The amount of condensed substance (about 1 mg in each experiment) was determined by GLC using an external standard (linear hydrocarbon). Assuming that Dalton's law of partial pressures when applied to the nitrogen stream saturated with the substance is valid, values of p_{sat} were calculated using the equation

$$p_{sat} = mRT_a/VM \tag{3}$$

where m is the mass of the transported substance; $V = V_{N_2} + V_{ketol}$, V_{N_2} is the volume of nitrogen; V_{ketol} is the volume contribution of ketol to the gaseous phase ($V_{N_2} \gg V_{ketol}$); T_a is the temperature of the soap film bubble flow meter. The vapor pressure p_{sat} at each saturation temperature was calculated from the amount of product collected within a definite time period. The value of p_{sat} was corrected for the small value of the residual vapor pressure at the temperature of condensation. The latter correction was calculated from a linear correlation between ln p_{sat} and T^{-1} obtained by iteration. We have checked experimental and calculation procedures with measurements of vapor pressures of l-alcohols.[8] It turned out that vapor pressures derived from the transpiration method were reliable within (1 to 3) %, and their accuracy was governed by reproducibility of the GLC analysis. However, in the case of the low-volatile ketol, the reproducibility of the GLC analysis has been on the level of 5 %.

Sublimation Enthalpy Measurements, Calorimetry. The enthalpy of sublimation of ketol was measured using a Calvet-type microcalorimeter MID-200[7] with the uncertainty to within ± 0.5 %.[9]

The molar enthalpy of sublimation of ketol was calculated using the equation:

$$\Delta_{sub}H^\circ_m = (K \cdot m)^{-1}\, M \int_{\tau=0}^{\tau} \Delta E \, d\tau \tag{4}$$

where m is the mass of the sublimed sample in vacuum; K is the calorimetric constant of the cell; ΔE is a thermo-electromotive force that is proportional to the difference to the temperature imbalance between the cell and the thermostat of the calorimeter at the time τ; $\int_{\tau=0}^{\tau} \Delta E \, d\tau$ is the total signal value recorded during the experiment.

The calorimetric constant of the cell was determined in series of experiments with naphthalene ($x = 0.9999$) for which sublimation enthalpy and heat-capacity change during sublimation at 298.15 K were taken as those: $\Delta_{sub}H^\circ_m = (72.6 \pm 0.6)$ $\mathrm{kJ \cdot mol^{-1}}$ and $\langle \Delta_{cr}^{g} C_p^\circ \rangle = -(34 \pm 2)$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ reported in ref 10.

Table 1. Saturated Vapor Pressure over the Liquid and the Crystalline Ketol Determined by the Knudsen Method

T^a / K	Δm^b / mg	t^c / s	k^d	Kn^e	p^f / Pa
Liquid $d^g = (0.4467 \pm 0.0004)$ mm					
308.22	9.87	16200	0.8451	3.34	1.23
313.05	9.24	10800	0.8609	2.45	1.71
317.95	14.08	10800	0.8829	1.66	2.56
322.97	10.48	5400	0.9093	1.16	3.73
325.33	8.47	3600	0.9252	0.97	4.47
327.45	10.43	3611	0.9394	0.81	5.42
330.40	12.94	3600	0.9585	0.67	6.64
Crystal $d^g = (0.8370 \pm 0.0004)$ mm, $\alpha = 0.005$					
289.55	4.00	21600	0.8043	21.3	0.129
290.90	4.59	19800	0.8009	17.0	0.163
292.45	4.19	15002	0.8019	14.2	0.196
294.44	6.22	18008	0.8085	11.6	0.241
295.86	8.45	19800	0.8159	9.49	0.296
297.42	9.06	18000	0.8123	8.03	0.352
297.92	9.57	18000	0.8187	7.67	0.369
299.90	9.60	14400	0.8228	6.12	0.466
300.83	12.87	16260	0.8293	5.24	0.545

[a] Temperature of saturation. [b] Mass loss. [c] Time of experiment. [d] Transmission probability factor. [e] Knudsen number. [f] Saturated vapor pressure corrected with respect to the isotropy failure theory and the condensation coefficient. [g] Diameter of the effusion orifice.

Vibration Spectra. The IR spectrum of crystalline ketol in the range from (400 to 3500) $\mathrm{cm^{-1}}$ (KBr pellets) and the IR spectra for solutions of ketol in CCl_4 (four sequential dilutions) were recorded with a Bruker Vertex 70 spectrometer at $T = 290$ K with resolution of 2 $\mathrm{cm^{-1}}$. The Raman spectrum in the range from (100 to 3500) $\mathrm{cm^{-1}}$ of crystalline ketol was recorded by a LabRam Raman microscope (HORIBA Jobin Yvon, Inc.) at $T = 290$ K.

Ab Initio Calculations. Calculation of the total energy of ketol conformers as well as of their IR and Raman spectra were performed with the Gaussian 03 Rev.C.02 series of the program[11] at the B3LYP/6-311G* level of theory.

Results

Saturated Vapor Pressure, Enthalpy of Sublimation, and Enthalpy of Vaporization of Ketol. The results of the effusion experiments p_{sat} on the crystalline and the liquid ketol in the temperature ranges from (289.6 to 300.8) K and from (308.2 to 330.4) K, respectively, are listed in Table 1. It should be mentioned that an anomalous increase of Δm has been observed in effusion experiments above 330.4 K, apparently due to decomposition of the sample in vacuum. But no traces of decomposition have been observed during the transpiration experiments at $T < 351.5$ K in the inert gas stream ($p_{N_2} \approx 10^5$ Pa), as well as the ketol being stable in the benzene solution during the sampling into injection port with a constant temperature of 523 K. In the transpiration experiments, the sample of ketol has remained liquid below its melting temperature 306.75 K down to 287.9 K. Thus, the p_{sat} values (see Table 2) were measured in the temperature ranges from (287.9 to 303.0) K and from (308.0 to 351.5) K, which covered the undercooled and the liquid state of the ketol.

Vapor pressures measured by effusion and transpiration techniques were fitted by

$$\ln(p_{sat}/\mathrm{Pa}) = A + B(T/\mathrm{K})^{-1} + C \ln\left[\left(\frac{T}{T_o}\right)/\mathrm{K}\right] \tag{5}$$

Table 2. Saturated Vapor Pressure over the Undercooled and the Liquid Ketol Determined by the Transpiration Method

T^a	m^b	$V(N_2)^c$	p^d	T^a	m^b	$V(N_2)^c$	p^d
K	mg	dm^3	Pa	K	mg	dm^3	Pa
287.9^e	1.35	105.5	0.17	333.3	1.45	2.22	8.16
293.2^e	1.51	67.80	0.29	336.2	1.07	1.50	8.86
298.0^e	1.78	47.09	0.49	337.4	1.13	1.50	9.49
303.0^e	1.13	21.17	0.71	338.4	1.01	1.21	10.42
308.0	0.97	12.20	0.99	340.2	1.49	1.56	11.85
311.1	1.08	10.18	1.34	341.3	1.14	1.14	12.49
313.1	0.88	7.20	1.53	342.6	1.63	1.36	14.80
316.2	1.20	7.15	2.09	344.6	1.30	1.00	16.13
318.2	0.89	4.82	2.34	345.4	1.38	0.93	18.32
321.2	1.04	4.28	3.05	347.0	1.03	0.71	18.08
323.3	0.96	3.03	3.95	348.4	1.64	1.03	19.81
325.2	1.21	3.72	4.03	348.6	1.09	0.67	20.13
328.2	0.66	1.52	5.40	350.5	1.40	0.70	24.99
330.2	1.29	2.81	5.67	351.5	0.94	0.49	23.78
331.3	1.39	2.86	6.05				

[a] Temperature of saturation. [b] Mass of transferred sample, condensed at $T = 243$ K. [c] Volume of nitrogen, used to transfer mass m of sample. [d] Vapor pressure at temperature T, calculated from m and the residual vapor pressure at the cooling temperature $T = 243$ K. [e] Temperature of undercooled liquid.

Table 3. Enthalpy of Sublimation of Ketol Determined by the Calorimetric Method

m^a	T	$\int_{\tau=0}^{\tau}\Delta E\,d\tau^b$	K^c	$\Delta_{cr}^{g}H_m^{\circ\,d}$
mg	K	mV·s	mV·s·J^{-1}	kJ·mol^{-1}
		Crystal		
18.79	303.11	1576.78	187.74 ± 0.66	87.74
17.75	303.14	1510.75	190.00 ± 1.42	87.94

[a] Mass of the sample corrected for buoyancy with the density of ketol $d = 1.2 \cdot 10^3$ kg·m^{-3}. [b] Total signal value recorded during the experiment. [c] Calorimetric constant of the cell. [d] $\langle\Delta_{cr}^{g}H_m^\circ(303.13\text{ K})\rangle = (87.8 \pm 1.8)$ kJ·mol^{-1}.

where $B = [\overline{\Delta_{cond}^{g}C_p^\circ}\cdot T_o - \Delta_{cond}^{g}H_m^\circ(T_o)]\cdot R^{-1}$, $C = \overline{\Delta_{cond}^{g}C_p^\circ}\cdot R^{-1}$, T_o is the average temperature of each method, $\underline{\Delta_{cond}^{g}H_m^\circ(T_o)}$ is the vaporization/sublimation enthalpy at T_o, $\overline{\Delta_{cond}^{g}C_p^\circ}$ is the average difference between the heat capacities of the condensed and vapor phase: $\overline{\Delta_{l}^{g}C_p^\circ} = -97.5$ J·K^{-1}·mol^{-1}, $\overline{\Delta_{cr}^{g}C_p^\circ} = -36.8$ J·K^{-1}·mol^{-1}.

The parameters of the equations $p_{sat} = f(T)$ for each method as well as the values of $\Delta_{l}^{g}H_m^\circ$ ($<T>$) and $\Delta_{cr}^{g}H_m^\circ$ ($<T>$) are listed in Table 4. Relative deviations of the experimental vapor pressure, measured by the effusion and the transpiration methods, from eq 5 are shown in Figure 1. Most of the experimental points deviate from the smoothing eq 5 by less than ± 5 %, however some points show scatter up to ± 10 %.

Calorimetric value of the enthalpy of sublimation has been measured with heat-conducting calorimeter (Table 3). Enthalpies of vaporization $\Delta_{l}^{g}H_m^\circ$ ($<T>$) and enthalpies of sublimation $\Delta_{cr}^{g}H_m^\circ$ ($<T>$) (see Tables 3 and 4) were adjusted to the temperatures 320.8 K and 298.2 K, respectively, with the use of the average differences between the heat capacities of the condensed and vapor state (see above). Moreover, the enthalpies of vaporization and sublimation at the triple point temperature were calculated in the same way, and the enthalpy of fusion has been calculated as their difference:

$$\Delta_{cr}^{l}H_m^\circ(306.75) = (21.4 \pm 1.3)\ \text{kJ}\cdot\text{mol}^{-1}$$

This value is in a good agreement with those obtained by the adiabatic calorimetry[2]: $\Delta_{cr}^{l}H_m^\circ(306.75) = (20.81 \pm 0.02)$ kJ·mol^{-1}.

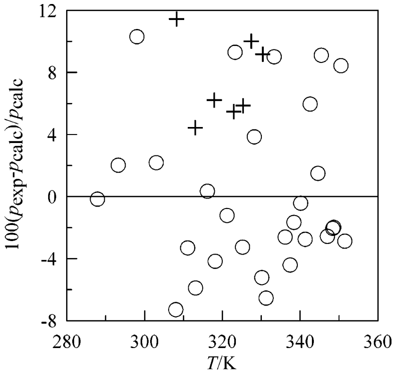

Figure 1. Deviation of the experimental vapor pressure data for the liquid and the undercooled ketol from the values calculated by eq 5. +, effusion method data; ○, transpiration method data.

In the dimerization process two intramolecular hydrogen bonds are changed to two intermolecular ones; therefore, $\Delta H \approx 0$ for this process. The entropy change in this process would be comparable to $-\Delta_{vap}S^\circ$.[12] So, the dimerization is an unfavorable process, and the vapor should consist of monomers. As a possible argument for the absence of the dimers in the ketol vapor could serve the behavior of ketol in the CCl_4 dilute solution studied by IR spectroscopy. Indeed, a narrow intensive band of the OH bond involving in the intramolecular hydrogen bond was detected in the region 3550 cm^{-1} while the band of the OH bond involved in intermolecular hydrogen bond in the region 3600 cm^{-1} was almost invisible.

Enthalpy of sublimation of ketol at $T = 298.15$ K derived in this work ($\Delta_{cr}^{g}H_m^\circ = 88.4 \pm 1.2$ kJ·mol^{-1}) together with the enthalpy of formation of crystalline ketol $\Delta_fH_m^\circ$ (cr, 298.15 K) $= -(597.6 \pm 2.4)$ kJ·mol^{-1} available from our recent study[2] provides now the standard enthalpy of formation for the substance in the gaseous state:

$$\Delta_fH_m^\circ\ (\text{g, 298.15 K}) = -(509.2 \pm 2.7)\ \text{kJ}\cdot\text{mol}^{-1}$$

The entropies of the liquid and the crystalline ketol available from our earlier work[2] and the enthalpies of vaporization and sublimation obtained in this study were used for the calculation of the entropies of ketol in the ideal gas state. According to the procedure described earlier,[13] the experimental gaseous entropy of ketol at 320.77 K, S_m° (g, 320.77) = (490.6 ± 2.3) J·K^{-1}·mol^{-1}, and at 298.15 K, S_m° (g, 298.15) = (475.0 ± 4.2) J·K^{-1}·mol^{-1} (Table S1, see Supporting Information) were calculated. A residual entropy $S^\circ(T \to 0) = R \ln 2$ caused by the existence of equivalent racemic mixture of two optical isomers in the condensed state was taken into account.

Table 4. Parameters of Equation 5 for the Temperature Dependence of Vapor Pressure for the Crystalline and the Liquid Ketol

method	temperature range	A	$-B$	$-C$	$\Delta_{cond}^{g}H_m^\circ(\langle T\rangle)$
			K		kJ·mol^{-1}
transpiration (liquid)	287.9 to 351.5 ($\langle T\rangle = 328.1$ K)	37.12 ± 0.17	11641 ± 57	11.7 ± 0.4	64.8 ± 0.5
effusion (liquid)	313.05 to 330.40 ($\langle T\rangle = 320.8$ K)	37.26 ± 0.46	11577 ± 147	11.7 ± 0.4	64.9 ± 1.2
effusion (crystal)	289.55 to 300.83 ($\langle T\rangle = 295.5$ K)	39.31 ± 0.66	11993 ± 194	4.4 ± 0.3	88.8 ± 1.6

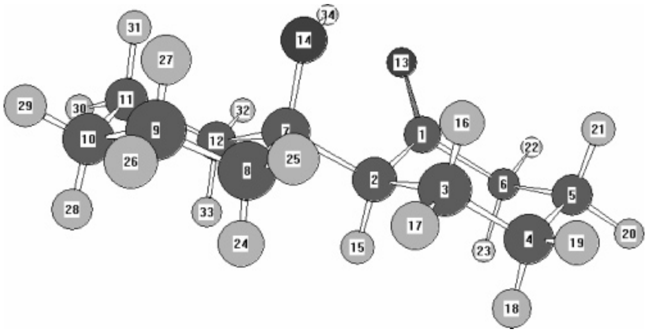

Figure 2. Most stable conformer of 2-(1′-hydroxycyclohexyl)cyclohexanone.

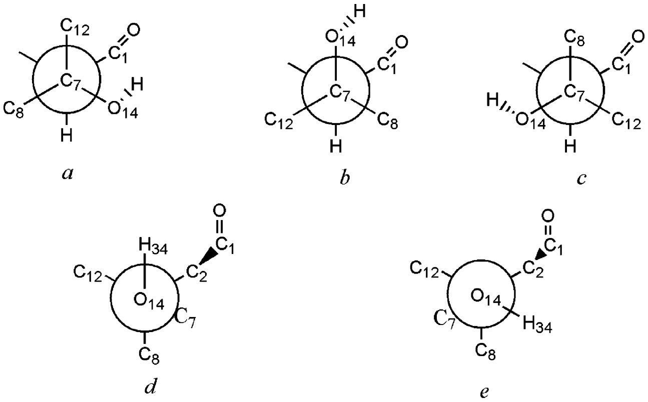

Figure 3. Newman projections of the conformers produced by rotation around C(2)−C(7) and C(7)−O(14) bonds: *a*, the most stable at 0 K; *b*, conformation of the ketol in the crystal lattice.

Thermodynamic Properties for 2-(1′-Hydroxycyclohexyl)-cyclohexanone in the Ideal Gas State. The procedure of statistical thermodynamic calculations of the thermodynamic properties in the ideal gas state was described in detail elsewhere.[13] Molar mass of ketol $M = 196.286\ \mathrm{g{\cdot}mol^{-1}}$ was calculated using atomic weights of elements recommended by IUPAC.[14]

Ketol has one chiral C-atom (Figure 2, atom C(2)). The following types of intramolecular motions are possible in a ketol molecule: hindered rotation of −OH group with the forming of two rotational isomers; hindered rotation of the rings around the C(2)−C(7) bond with the forming of three rotational isomers (Newman projections of the rotational isomers are shown in Figure 3); and inversion of "cyclohexanol" and "cyclohexanone" rings with the forming of the equatorial and axial "chair" ring isomers and five "twist" isomers in each case. Relative energies of the conformers $E_i - E_0$ (E_0 is the energy of conformer *b*, see Figure 3) together with the mole fractions of the conformers at 298.15 K are listed in Table 5. Optimization of geometry and calculation of total energy of each the conformer was carried out by quantum-mechanical methods. Zero-point vibration energies were found with the use of the calculated vibration frequencies scaled by a factor χ from eq 6 described below (Table S2, see Supporting Information). In the calculation of the mole fractions, it was assumed that all types of intramolecular motions are independent.

All the conformers belong to C_1 group of symmetry. The products of the principal moments of inertia ($I_AI_BI_C$) are listed in Table S3 (see Supporting Information).

Experimental absorption bands of Raman (Figure 4) and IR spectra for the crystalline ketol and its IR spectrum in CCl_4 solution (Figure 5) are listed in Table 6. From the comparison of the experimental and calculated spectra, it was assumed that crystal of the ketol is formed by molecules in the *b* conformation. The accordance between the experimental and the calculated values for the bands observed in the experimental spectra was found with the use of calculated and observed intensities of the absorption Raman and IR bands. The scaling factors $\chi = w_{\mathrm{exp}}/w_{\mathrm{calc}}$ for the range (100 to 3500) cm^{-1} were fitted by the following equation:

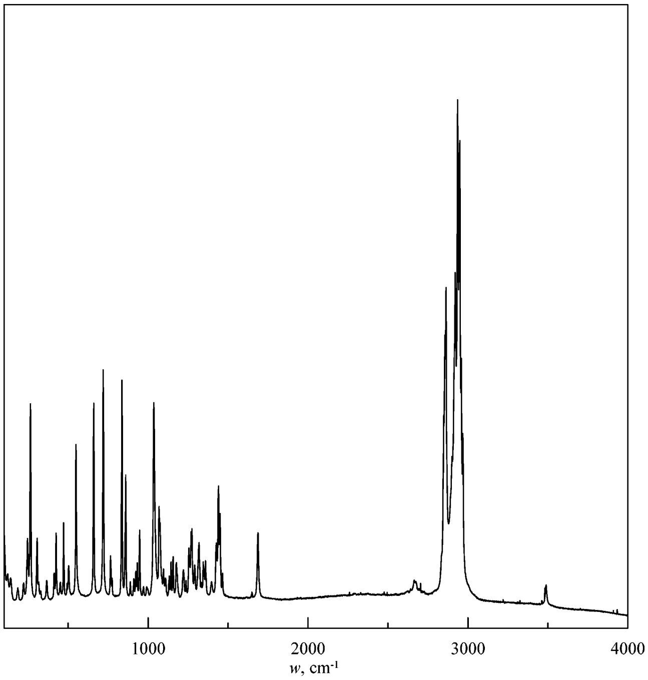

Figure 4. Raman spectrum of crystalline ketol.

Table 5. Differences in the Energies of the Conformers of 2-(1′-Hydroxycyclohexyl)cyclohexanone from ab initio Calculations

type of conformational motion	ΔH (0 K) kJ·mol^{-1}	x_i (298.15 K)
hindered rotation around C(7)−O(14) bond	0	$99.998{\cdot}10^{-2}$
	26.6	$2.15{\cdot}10^{-5}$
hindered rotation around C(2)−C(7) bond	0	$44.15{\cdot}10^{-2}$
	−0.5	$55.63{\cdot}10^{-2}$
	13.1	$0.22{\cdot}10^{-2}$
inversion of C(7)C(8)C(9)C(10)C(11)C(12) ring	0	$91.56{\cdot}10^{-2}$
	22.5	$11.5{\cdot}10^{-5}$
	26.8	$1.98{\cdot}10^{-5}$
	24.9	$4.27{\cdot}10^{-5}$
	45.8	$9.30{\cdot}10^{-9}$
	22.2	$13.1{\cdot}10^{-5}$
	5.9	$9.19{\cdot}10^{-2}$
inversion of C(1)C(2)C(3)C(4)C(5)C(6) ring	0	$98.94{\cdot}10^{-2}$
	25.4	$3.13{\cdot}10^{-4}$
	11.4	$9.89{\cdot}10^{-3}$
	40.2	$9.13{\cdot}10^{-8}$
	28.4	$10.5{\cdot}10^{-6}$
	25.5	$3.35{\cdot}10^{-5}$
	19.0	$4.66{\cdot}10^{-4}$

$$\chi = (1.025 \pm 0.002) - (4.22 \pm 0.14){\cdot}10^{-5}(w_{\mathrm{calc}}/\mathrm{cm^{-1}}) \quad (6)$$

The vibration frequencies invisible both in IR and Raman spectra were assessed with the help of quantum-mechanical calculations and the scaling factors χ from eq 6. The set of selected fundamental frequencies for the *b* conformer obtained by combining the experimental and theoretical results are listed in Table 6.

Thermodynamic properties of ketol in the ideal-gas state in the temperature range (50 to 1000) K are listed in Table 7. The calculated entropy of ketol in the ideal gas state was S°_{m}(320.8

Table 6. Experimental and Calculated (B3LYP/6-311G*) Fundamental Frequencies for the *b* Conformer of Ketol

experimental frequencies in cm^{-1}					experimental frequencies in cm^{-1}				
IR	IR, soln in CCl_4	Raman	ab initio, scaled	selected	IR	IR, soln in CCl_4	Raman	ab initio, scaled	selected
			61	61	1216	1216	1223	1246	1216
			91	91	1236	1235	1237	1271	1229
		122	113	113	1258	1257	1255	1293	1257
		141	133	133				1296	1257
		186	184	186	1267	1263	1270	1304	1263
		222	217	222	1275	1273	1275	1310	1273
		246	235	246	1295	1298	1292	1325	1298
		264	264	264	1311	1309		1348	1309
		306	307	306		1319	1319	1355	1319
		316	319	316	1325			1360	1319
		328	331	328			1333	1376	1333
		367	369	367	1341	1345		1379	1345
420	415	414	419	414		1355	1345	1376	1345
425	423	425	428	423			1350	1391	1355
455		452	454	452				1394	1355
473	472	473	479	472	1351			1396	1355
498		495	503	501			1359	1404	1359
	501	504	504	501	1401	1393	1397	1442	1393
562	549	550	551	549	1428	1426	1428	1483	1428
			615	615				1487	1428
661	659	661	666	659	1440	1434	1440	1497	1434
			670	659				1501	1434
719		720	720	719	1449	1448	1449	1507	1448
765		766	760	766				1507	1448
			783	783				1510	1448
834	831		843	831	1465	1460	1466	1519	1460
	837	837	845	837				1524	1460
855	854	857	865	854	1689	1699	1688	1763	1699
860	860	861	869	860	2840		2848	2985	2848
885	886	889	902	890	2861		2856	2994	2856
910	910	912	921	910				3012	2863
923	920	923	934	923				3013	2863
947	947	947	949	947		2892		3022	2892
			956	947				3025	2902
969		972	991	973				3026	2902
		992	1007	992		2902	2901	3031	2902
			1044	1026				3035	2902
			1046	1028			2915	3039	2915
1041		1036	1048	1041			2921	3051	2921
			1050	1059	2932	2938		3062	2938
1066		1069	1082	1064				3064	2938
1080	1081	1075	1097	1081			2936	3069	2938
1100	1103	1097	1120	1095				3070	2938
1113	1110	1110	1126	1103	2944		2949	3080	2944
1132	1129	1133	1152	1129				3085	2944
1146	1143	1144	1167	1143			2959	3090	2944
1157	1157	1157	1187	1157			2969	3101	2959
1182	1179	1183	1206	1179	3488	3532	3489	3714	3532

Table 7. Thermodynamic Properties of 2-(1′-Hydroxycyclohexyl)cyclohexanone in the Ideal Gas State

T / K	S°_m / $J \cdot K^{-1} \cdot mol^{-1}$	$C^\circ_{p,m}$ / $J \cdot K^{-1} \cdot mol^{-1}$	$\Delta_0^T H^\circ_m/T$ / $J \cdot K^{-1} \cdot mol^{-1}$	$-\Delta_0^T G^\circ_m/T$ / $J \cdot K^{-1} \cdot mol^{-1}$	$-\Delta_f H^\circ_m$ / $kJ \cdot mol^{-1}$	$\Delta_f G^\circ_m$ / $kJ \cdot mol^{-1}$
50	268.8	53.7	40.3	228.5	454.0	−420.8
100	315.8	86.4	55.0	260.9	468.9	−381.3
150	357.5	121.6	71.3	286.2	480.1	−335.0
200	397.5	158.7	88.5	309.0	490.5	−285.1
273.15	455.7	218.7	115.2	340.5	505.0	−207.5
298.15	475.7	240.4	124.7	351.0	509.6	−180.1
300	477.2	242.0	125.5	351.8	509.9	−178.1
400	558.8	328.2	165.5	393.3	525.7	−65.0
500	640.5	405.3	205.9	434.6	537.1	51.7
600	720.3	469.8	244.7	475.6	544.7	170.2
700	796.8	522.7	280.8	516.1	548.9	289.7
800	869.5	566.0	313.8	555.7	550.3	410.2
900	938.3	601.7	343.9	594.5	549.4	529.5
1000	1003.3	631.3	371.2	632.1	546.7	649.3

K) = 494.0J·K^{-1}·mol^{-1} and S°_m(298.2 K) = 475.7 J·K^{-1}·mol^{-1} (Table S1, see Supporting Information).

Equilibrium of Cyclohexanone Dimerization and Equilibrium of Ketol Dehydration in the Vapor Phase. In our previous work, equilibrium of reaction I in the liquid phase $K^\circ_{r(1)}$(332.1 K) = 4.8·10^{-2} was already reported.[2] The values of the saturated vapor pressure of ketol obtained in this work together with those for cyclohexanone[15] allows now to estimate the equilibrium

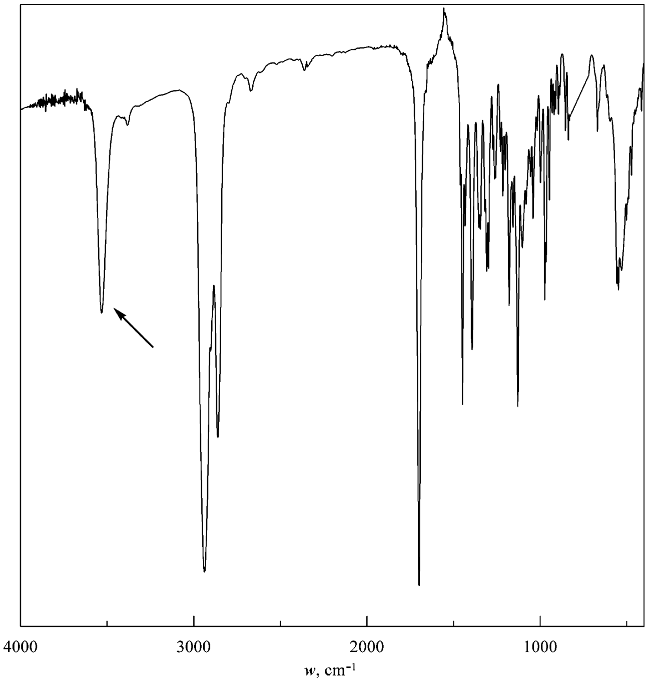

Figure 5. IR spectrum of ketol in CCl_4 solution. The band of the OH-bond adjacent to the intramolecular hydrogen bond is marked by an arrow.

constant $K^\circ_{r(1)}$ for reaction I in the vapor phase at 332.1 K:

$$K^\circ_{r(1)}\ (\text{g, 332.1 K}) = K^\circ_{r(1)}\ (\text{liq, 332.1 K}) = \frac{p_{\text{ketol}}}{p_{\text{cyclohexanone}}}10^5 = 2.4\cdot10^{-3} \quad (7)$$

where p_i are the saturated vapor pressures for the pure substances.

This constant has been also calculated using the thermodynamic properties from Table 7 for ketol $\Delta_f G^\circ_m$ (ketol, gas, 332.1 K) = −138.5 kJ·mol^{-1} and those for cyclohexanone $\Delta_f G^\circ_m$ (cyclohexanone, gas, 332.1 K) = −76.1 kJ·mol^{-1}:[15]

$$K^\circ_{r(1)}\ (\text{gas, 332.1 K}) = 6.9\cdot10^{-3}$$

The equilibrium constants of reaction I derived from experimental and theoretical methods are in close agreement, and the value of $K^\circ_{r(1)}$ in the vapor phase is 1 order of magnitude less than that in the liquid phase.

It is known[1] that the ketol during the caprolactam production undergoes further dehydration according to reactions II and III leading to formation of 2-(1-cyclohexenyl)cyclohexanone and 2-(1-cyclohexylidene)cyclohexanone:

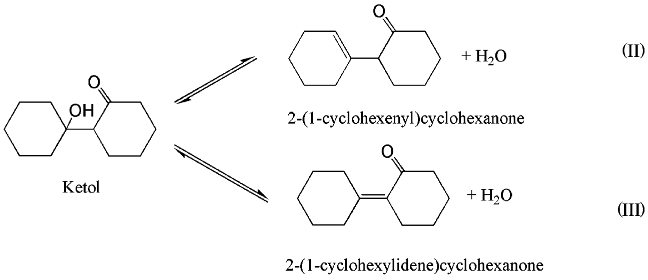

Table 8. Thermodynamic Properties of the Participants in Reaction II in the Ideal Gas State (T = 298.15 K)

property	ketol	2-(1-cyclohexenyl)cyclohexanone[16]	H_2O[15]
$-\Delta_f H^\circ_m$/kJ·mol^{-1}	509.6	217.2	241.8
S°_m/J·K^{-1}·mol^{-1}	475.7	492.4	188.8

These reactions are reversible, and 2-(1-cyclohexenyl)cyclohexanone is formed during the dehydration in larger amount than 2-(1-cyclohexylidene)cyclohexanone. The thermodynamic characteristics of reaction II in the vapor phase at 298.15 K were calculated with the use of the thermodynamic properties for ketol in the ideal-gas state listed in Table 7 and those for water[15]and 2-(1-cyclohexenyl)cyclohexanone[16] (Table 8). A residual entropy $S^\circ(T \rightarrow 0) = R \ln 2$ caused by the existence of equivalent racemic mixture of two optical isomers of 2-(1-cyclohexenyl)cyclohexanone in the condensed state was taken into account:

$$\Delta_{r(2)}H^\circ_m(298.15\ \text{K}) = 50.6\ \text{kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{r(2)}S^\circ_m(298.15\ \text{K}) = 205.5\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$K^\circ_{r(2)} = 74.01$$

At this temperature and $p = 10^5$ Pa, the conversion of ketol is rather low: equilibrium mole fractions of the participants are x(ketol) = 0.947; x(2-(1-cyclohexenyl)cyclohexanone) = $2.65\cdot10^{-2}$; $x(H_2O) = 2.65\cdot10^{-2}$. But since the reaction is endothermic, conversion of the ketol will increase with the increase of temperature.

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Supporting Information Available:

Three additional tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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