

Thermodynamic Properties for 2-(1'-Hydroxycyclohexyl)cyclohexanone and Equilibrium of Dimerization of Cyclohexanone

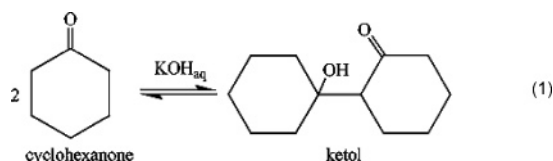
Marina P. Shevelyova,[†] Gennady J. Kabo,^{*,†} Andrey V. Blokhin,[†] Andrey G. Kabo,[†] Joseph A. Jursha,[‡] and Anna A. Rajko[‡]

Chemical Department, Belarusian State University, Leningradskaya 14, Minsk 220050, Belarus, and "Grodno Azot", Kosmonavtov av. 100, Grodno 230013, Belarus

Thermodynamic properties of 2-(1'-hydroxycyclohexyl)cyclohexanone (ketol) are reported. The investigated compound is a byproduct from the caprolactam manufacture. The heat capacity of ketol was measured by vacuum adiabatic calorimetry ($T = 5$ K to $T = 310$ K) and by differential scanning calorimetry ($T = 294$ K to $T = 370$ K). The fusion temperature $T_{\text{fus}} = 306.75$ K and the mole fraction of the ketol sample ($x = 0.9982$) were found by fractional melting analysis. The molar enthalpy of fusion $\Delta_{\text{fus}}H_{\text{m}}^{\circ} = (20.81 \pm 0.02)$ kJ·mol⁻¹ was determined in the adiabatic calorimeter. The standard molar thermodynamic functions of ketol in the condensed state were obtained with the use of these calorimetric measurements. The standard molar enthalpy of combustion of ketol $\Delta_c H_{\text{m}}^{\circ}(\text{cr}, 298.15 \text{ K}) = -(6963.0 \pm 1.8)$ kJ·mol⁻¹ was found by bomb calorimetry, and the standard molar enthalpy of formation $\Delta_f H_{\text{m}}^{\circ}(\text{cr}, 298.15 \text{ K}) = -(597.6 \pm 2.4)$ kJ·mol⁻¹ was derived. The equilibrium of dimerization of cyclohexanone with ketol formation was investigated in the temperature range 294 K to 367 K. The equilibrium constants (K_{a}) were obtained at five temperatures, and the enthalpy of the reaction at the average temperature $\Delta_r H_{\text{m}}(330.5 \text{ K}) = -(34.4 \pm 3.3)$ kJ·mol⁻¹ was derived.

Introduction

2-(1'-Hydroxycyclohexyl)cyclohexanone (ketol) is one of the byproducts of caprolactam production, and it is formed during cyclohexane oxidation and cyclohexanol dehydrogenation to cyclohexanone (reaction 1):



The reaction is an initial stage of the other bicyclic ketones¹ formation influencing the economics of caprolactam production.

Ketol is dehydrated easily at temperatures above 373 K with the formation of bicyclic ketones. Efimova et al.² investigated the equilibrium of reaction 1 in the presence of alkali solution with butan-1-ol as the solvent in the temperature range (303.15 to 343.15) K, but they did not give information about the equilibrium concentrations of the reagents and the method used to calculate the equilibrium constants. The enthalpy of reaction 1

$$\Delta_r H^{\circ}(323.15 \text{ K}) = -47.8 \text{ kJ} \cdot \text{mol}^{-1}$$

adduced in ref 2 does not correspond with the value

$$\Delta_r H^{\circ}(323.15 \text{ K}) = -(26.6 \pm 7.7) \text{ kJ} \cdot \text{mol}^{-1}$$

derived from the equilibrium constants that are presented in the article.

* Corresponding author. E-mail: kabo@bsu.by.

[†] Belarusian State University.

[‡] "Grodno Azot".

With the purpose of thermodynamic investigation of reaction 1, the heat-capacity of 2-(1'-hydroxycyclohexyl)cyclohexanone was measured in the temperature range (5 to 370) K, and the thermodynamic properties of ketol in the condensed state were calculated. The enthalpy of formation for ketol was determined by bomb calorimetry. The equilibrium of reaction 1 with aqueous alkali solution as a catalyst was investigated. The enthalpy of reaction 1 was obtained and compared with the calorimetric data.

Experimental Section

Chemicals. A sample of 2-(1'-hydroxycyclohexyl)cyclohexanone was prepared by the procedure described in ref 1 and was purified by thrice-repeated recrystallization from petroleum ether (fraction with $T_{\text{boil}} = (323 \text{ to } 333)$ K). Thereafter, it was sublimated from the melt and crystallized on a glass trap at $T = (313 \text{ to } 318)$ K and $p = 267$ Pa. The final mole fraction purity of the sample was 0.9982, determined as described below.

Apparatus and Procedure. The low-temperature heat capacities in the temperature range (5 to 310) K and the enthalpy of fusion of ketol were measured in the vacuum adiabatic calorimeter (AC) TAU-1 constructed by VNIIFTRI (Moscow) as previously described.^{3–5} The crystalline sample ($m = 0.9378$ g) was loaded into a stainless steel container of 1.0 cm³ volume. The container headspace was filled with helium to the pressure about 6 kPa to improve the heat exchange. The container was sealed with an indium ring. The temperature was measured with an iron–rhodium resistance thermometer ($R_0 = 101.83 \text{ } \Omega$) located on the inner surface of the adiabatic shield and calibrated for ITS-90 by VNIIFTRI (Moscow). Adiabatic conditions within ± 0.001 K were maintained with a four-junction differential thermocouple {(Cu (mole fraction 0.999) + Fe (mole fraction 0.001))-to-chromel} that indicated of the temperature difference between the shield and the calorimetric cell.

The reliability of the heat capacity measurements had been verified previously with benzoic acid^{6,7} (K-1 grade, mass fraction ≥ 0.99995) and high-purity copper⁸ (mass fraction ≥ 0.99995). The estimated uncertainty of the molar heat capacity measurements was $\pm 0.4\%$ in the temperature range (40 to 320) K. The uncertainty increased at $T < 40$ K and finally reached $\pm 2\%$ in the temperature range (5 to 10) K. The difference between the values of $C_{s,m}$ and $C_{p,m}$ was considered to be negligible because of the low vapor pressure of ketol.

The heat capacity of ketol in the temperature range (294 to 370) K was measured using an improved automatic scanning calorimeter of the heat bridge type⁹ (DSC). The calorimeter was calibrated with high-purity copper (mass fraction ≥ 0.99995). The expanded uncertainty of the heat capacity measurements was estimated to be $\pm 2\%$. The container with the sample ($m = 0.9991$ g) was hermetically sealed in a vacuum. The values of the heat capacity were obtained with temperature steps from (0.05 to 0.1) K. The average heating rate was $0.8\text{ K}\cdot\text{min}^{-1}$.

The enthalpy of combustion for ketol was determined by the procedure described earlier.⁴ Three isoperibolic calorimeters (A, B, and C) with isothermal water shields and static bombs were used for the measurements. The temperatures of the shields were kept constant within ± 0.01 K. The reproducibility of the measurements of the combustion energy was $\pm 0.02\%$.⁴ Reference benzoic acid (K-1, VNIIM, St-Petersburg) was used for calibration of the calorimeters; its specific energy of combustion was

$$\Delta_c U_{BA}^0 = -(26434.4 \pm 0.6)\text{ J}\cdot\text{g}^{-1}$$

based on mass in a vacuum and combusted under certificated conditions. The energy equivalents of the calorimeters were

$$W_A = (14890.0 \pm 2.2)\text{ J}\cdot\text{K}^{-1}$$

$$W_B = (14939.4 \pm 3.0)\text{ J}\cdot\text{K}^{-1}$$

$$W_C = (14709.9 \pm 2.3)\text{ J}\cdot\text{K}^{-1}$$

Measurements on two samples were made with a terylene ampule. The energy of combustion of terylene ($\text{C}_{10}\text{H}_8\text{O}_4$, $\rho = 1.38\text{ g}\cdot\text{cm}^{-3}$) was determined in five individual experiments:

$$\Delta_c U_{\text{ter}}^0 = -(22879.7 \pm 11.1)\text{ J}\cdot\text{g}^{-1}$$

Sums of the Washburn corrections for conversion of the energy of combustion to the standard state were calculated as previously described.¹⁰ Correction for ignition was 2.0 J in each experiment.

The samples were weighed on a Mettler Toledo AG 245 balance. The uncertainty of the weighing was $\pm 5\cdot 10^{-5}\text{ g}$. The masses of the samples were converted to the vacuum masses; the density of crystalline ketol ($\rho_{\text{cr}} = 1.14\text{ g}\cdot\text{cm}^{-3}$) at 292 K was determined with a pycnometer, with a saturated aqueous solution of ketol being used as a working liquid.

Reaction 1 takes place on the interface between an alkali solution (as catalyst) and an organic phase. The equilibrium of reaction 1 was studied in the range (294 to 367) K, with the choice of the temperature range determined by the instability of ketol at higher temperatures and long duration of equilibrium establishment at lower temperatures. Cyclohexanone (or its mixtures with ketol with higher mole fractions of ketol than the equilibrium ones) and aqueous solution of KOH (mass fraction 5%) were loaded in a vessel in the volume ratio of 1 to 2.¹ The uncertainty of the temperature measurement was $\pm$

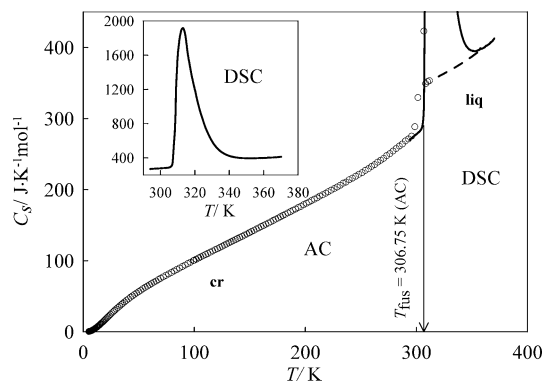


Figure 1. Experimental heat capacity ($C_{s,m}$) of 2-(1'-hydroxycyclohexyl)-cyclohexanone in the condensed state in the range (5 to 370) K. AC is the range of adiabatic calorimetry; DSC is the range of differential scanning calorimetry. Inset: experimental heat capacity measured by differential scanning calorimetry

0.25 K . The relative content of ketol and cyclohexanone in organic phase was determined by gas chromatography (TSVET-100 using N_2 as carrier gas and a flame ionization detector). Samples of the organic phase for chromatography were taken with a microsyringe in fixed time intervals. The mixtures were analyzed on a 0.4 m glass column, filled with 15% Reoplex on chromatron N-AW-HMDS. Temperature of the evaporator and the column was 403 K . The relation of molar concentrations of cyclohexanone and ketol in the organic phase was determined using a calibration factor for calculation of composition according to the areas of the chromatographic peaks. Equilibrium was assumed when the ratio of ketol peak areas to cyclohexanone peak areas with time remained constant.

Results and Discussion

The measured molar heat capacities of ketol in the range (5 to 370 K) are shown in Figure 1. The values obtained by adiabatic calorimetry are presented in Table 1. The temperature intervals of the values of $C_{s,m}$ are close to the difference between the mean temperatures of two successive experiments in the series of measurements.

Only one anomaly attributed to melting was found in the curve $C_{s,m} = f(T)$. To obtain a completely crystalline sample in the calorimeter, a liquid sample was cooled from 310 K to 100 K , and then it was heated from 100 K to about 290 K and was kept at this temperature for (8 to 10) h until the spontaneous heat evolution due to crystallization had stopped. The temperature interval of fusion of the sample was (294 to 308 K) in the adiabatic calorimeter and (303 to 359 K) in the differential scanning calorimeter.

The experimental heat capacities of the phases were fitted by the polynomials:

$$C_{p,m}(\text{cr})/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) = 227.32 - 1.0032(T/\text{K}) + 3.9432\cdot 10^{-3}(T/\text{K})^2 \quad (1)$$

$$C_{p,m}(\text{liq})/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) = 657.79 - 2.6379(T/\text{K}) + 5.3279\cdot 10^{-3}(T/\text{K})^2 \quad (2)$$

obtained in the temperature ranges (251 to 294 K) for the crystalline state and (308 to 312 K) (results of adiabatic calorimetry) and (359 to 370 K) (results of differential scanning calorimetry) for the liquid state. The difference between the values of the molar heat capacity in the range (294 to 303 K) obtained by differential scanning calorimetry and the values of

Table 1. Experimental Molar Heat Capacities ($C_{s,m}$) at Vapor-Saturation Pressure for 2-(1'-Hydroxycyclohexyl)cyclohexanone ($R = 8.31447 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)

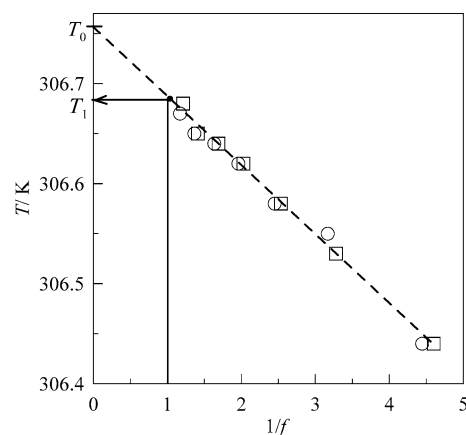
$\langle T \rangle$	$C_{s,m}^a$	$\langle T \rangle$	$C_{s,m}^a$	$\langle T \rangle$	$C_{s,m}^a$	$\langle T \rangle$	$C_{s,m}^a$
K	R	K	R	K	R	K	R
Series 1: Crystal							
99.86	12.10	143.17	16.16	186.58	20.34	239.45	25.74
101.89	12.29	145.31	16.38	188.92	20.59	242.37	26.01
103.96	12.50	147.42	16.56	191.24	20.79	245.30	26.33
106.00	12.69	149.52	16.77	193.62	21.04	248.20	26.66
108.09	12.89	149.69	16.78	196.06	21.24	251.09	26.94
110.22	13.08	151.77	17.00	198.49	21.53	253.97	27.32
112.32	13.27	153.83	17.17	200.89	21.75	256.81	27.61
114.47	13.49	155.94	17.40	203.28	21.97	259.61	27.99
116.67	13.68	158.11	17.58	205.65	22.23	262.37	28.29
118.84	13.90	160.26	17.81	208.08	22.45	265.10	28.72
120.97	14.07	162.40	17.99	210.57	22.68	267.80	29.04
123.07	14.28	164.58	18.22	213.04	22.97	270.46	29.36
125.14	14.48	166.82	18.41	215.63	23.20	273.22	29.82
127.19	14.68	169.05	18.62	218.36	23.46	276.10	30.16
129.21	14.87	171.25	18.85	220.54	23.71	278.95	30.59
131.21	15.06	173.43	19.07	223.28	23.98	281.77	31.01
133.17	15.24	175.59	19.26	226.00	24.24	284.57	31.44
135.12	15.42	177.74	19.48	228.71	24.51	287.35	31.78
137.05	15.59	179.87	19.70	231.37	24.80	290.11	32.30
138.96	15.79	181.98	19.89	234.03	25.16	292.83	32.64
141.00	15.97	184.22	20.13	236.67	25.35	295.66	33.11
Series 1: Liquid							
306.72	50.88	308.34	42.21	310.04	42.28	311.73	42.51
Series 2: Crystal							
274.83	29.97	282.51	31.08	287.51	31.86	292.40	32.65
277.41	30.36	285.02	31.51	289.97	32.19	294.18	32.89
279.97	30.76						
Series 3: Crystal							
5.156	0.06411	13.09	0.9042	29.78	3.874	63.72	8.414
5.413	0.07408	13.65	0.9946	31.31	4.121	65.71	8.599
5.681	0.08589	14.26	1.093	32.81	4.360	67.67	8.841
5.967	0.09841	14.87	1.190	34.25	4.605	69.76	9.063
6.289	0.1165	15.47	1.288	35.69	4.813	72.08	9.302
6.618	0.1368	16.12	1.402	37.25	5.057	74.55	9.565
6.939	0.1608	16.79	1.523	38.95	5.326	76.99	9.804
7.272	0.1881	17.47	1.643	40.79	5.576	79.43	10.05
7.692	0.2224	18.17	1.771	42.67	5.860	81.9	10.30
8.087	0.2605	18.86	1.900	44.41	6.084	84.37	10.56
8.514	0.3036	19.61	2.029	46.25	6.347	86.86	10.80
8.974	0.3491	20.52	2.194	48.19	6.575	89.34	11.07
9.402	0.3977	21.52	2.383	50.08	6.811	91.79	11.29
9.859	0.4527	22.54	2.569	51.93	7.031	94.27	11.55
10.32	0.5108	23.56	2.763	53.83	7.296	96.74	11.78
10.80	0.5707	24.68	2.967	55.82	7.536	99.23	12.06
11.34	0.6478	25.89	3.197	57.81	7.744	101.72	12.28
11.91	0.7310	27.12	3.408	59.76	7.963	104.22	12.52
12.50	0.8158	28.37	3.626	61.73	8.182		

^a Average heat capacity at the mean temperature of an experiment $\langle T \rangle$.**Table 2. Melted Fraction (f) as a Function of Temperature**

Series 1				Series 2			
T/K	f	T/K	f	T/K	f	T/K	f
306.44	0.2250	306.64	0.6120	306.44	0.2174	306.64	0.5914
306.55	0.3157	306.65	0.7326	306.53	0.3050	306.65	0.7077
306.58	0.4082	306.67	0.8540	306.58	0.3943	306.68	0.8251
306.62	0.5102			306.62	0.4929		

adiabatic calorimetry extrapolated by polynomial (1) did not exceed 1.3 %.

The temperature of fusion $T_{\text{fus}} = (306.75 \pm 0.01) \text{ K}$ and the mole fraction purity $x = (0.9982 \pm 0.0001)$ of ketol were obtained from the fractional melting experiments. The results are presented in Table 2. The plot of the equilibrium temperature as a function of $1/f$ (f is the melted fraction at the temperature T) is shown in Figure 2. The melted fractions were determined

**Figure 2.** Results of the fractional-melting experiments; $\circ$, results of series 1; $\square$, results of series 2; $\bullet$, completely melted ketol sample; T_1 , fusion temperature of the ketol sample used (mole fraction 0.9982); T_0 , fusion temperature of the pure substance.**Table 3. Determination of the Molar Enthalpy of Fusion for 2-(1'-Hydroxycyclohexyl)cyclohexanone**

$T_{\text{start}}/\text{K}$	T_{end}/K	Q^a/J	$\Delta_{\text{fus}}H_m^\circ/\text{J}\cdot\text{mol}^{-1}$
293.16	309.47	124.366	20807
293.35	309.85	124.910	20837
293.85	309.66	123.787	20809
293.04	308.80	123.308	20792
			$\langle \Delta_{\text{fus}}H_m^\circ \rangle = (20812 \pm 29)^b$

^a Q is the energy needed for heating the sample from T_{start} to T_{end} .^b Average value.

after subtraction of the regular part of the heat capacity. The experimental values were fitted by the van't Hoff equation:

$$T = T_{\text{fus}} - \left\{ \frac{RT_{\text{fus}}^2}{\Delta_{\text{fus}}H_m^\circ} (1-x) \right\} \frac{1}{f} = (306.75 \pm 0.01) - (0.0683 \pm 0.0037) \frac{1}{f} \quad (3)$$

The temperature of fusion by differential scanning calorimetry was considered to be the value obtained by the intersection of curve $C_{s,m}(\text{ketol,cr}) = f(T)$ and the tangent to the rising branch of the melting peak. The value obtained $T_{\text{fus}} = (306.9 \pm 0.2) \text{ K}$ is in good agreement with the results of adiabatic calorimetry.

The enthalpy of fusion by adiabatic calorimetry $\Delta_{\text{fus}}H_m^\circ = (20.81 \pm 0.02) \text{ kJ}\cdot\text{mol}^{-1}$ was obtained by averaging the results of four independent single-step experiments presented in Table 3. In each experiment the sample was heated from a temperature $\approx 13 \text{ K}$ below the melting point to a temperature of 3 K above the melting point. The enthalpy of fusion was calculated by the equation:

$$\Delta_{\text{fus}}H_m^\circ = \frac{Q}{m} - \int_{T_{\text{start}}}^{T_{\text{fus}}} C_{p,m}(\text{cr}) dT - \int_{T_{\text{fus}}}^{T_{\text{end}}} C_{p,m}(\text{liq}) dT \quad (4)$$

where $C_{p,m}(\text{cr})$ and $C_{p,m}(\text{liq})$ are the molar heat capacities of crystal and liquid (eqs 1 and 2), Q is the energy needed for heating the sample from T_{start} to T_{end} , m is the mass of the sample, and M is the molar mass of ketol.

The enthalpy of fusion $\Delta_{\text{fus}}H_m^\circ = (20.69 \pm 0.41) \text{ kJ}\cdot\text{mol}^{-1}$ by differential scanning calorimetry was determined by integration of the excess heat capacity over the fusion area. The values of the enthalpy of fusion obtained by both the methods agree within their respective uncertainties.

Table 4. Molar Thermodynamic Functions for 2-(1'-Hydroxycyclohexyl)cyclohexanone ($R = 8.31447 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)

T/K	$C_{p,m}/R$	$\Delta_0^T H_m^o/RT$	$\Delta_0^T S_m^o/R$	Φ_m^o/R
Crystal				
5	0.0597	0.0149	0.0200	0.00505
10	0.4701	0.1203	0.1602	0.0399
15	1.212	0.3549	0.4842	0.1293
20	2.102	0.6792	0.9533	0.2741
25	3.027	1.056	1.522	0.4655
30	3.907	1.459	2.152	0.6934
35	4.712	1.867	2.816	0.9490
40	5.472	2.271	3.495	1.225
45	6.164	2.665	4.180	1.515
50	6.805	3.048	4.863	1.816
60	7.994	3.775	6.211	2.436
70	9.087	4.456	7.526	3.070
80	10.12	5.100	8.807	3.707
90	11.11	5.713	10.06	4.343
100	12.11	6.303	11.28	4.976
110	13.06	6.874	12.48	5.604
120	14.00	7.429	13.66	6.226
130	14.94	7.971	14.81	6.842
140	15.88	8.502	15.95	7.452
150	16.82	9.025	17.08	8.057
160	17.77	9.541	18.20	8.656
170	18.74	10.05	19.30	9.250
180	19.71	10.56	20.40	9.839
190	20.68	11.07	21.49	10.42
200	21.65	11.57	22.58	11.00
210	22.64	12.08	23.66	11.58
220	23.65	12.58	24.73	12.15
230	24.67	13.08	25.81	12.72
240	25.73	13.59	26.88	13.29
250	26.85	14.10	27.95	13.86
260	28.05	14.61	29.03	14.42
270	29.34	15.13	30.11	14.98
280	30.73	15.66	31.20	15.54
290	32.23	16.21	32.31	16.10
300	33.86 ^b	16.77	33.43	16.66
306.75	35.04 ^b	17.16	34.19	17.04
Liquid				
306.75	42.09 ^b	25.32	42.35	17.04
310	42.34 ^c	25.50	42.80	17.30
320	43.21 ^c	26.03	44.16	18.12
330	44.20 ^c	26.57	45.50	18.93
340	45.32 ^c	27.10	46.84	19.73
350	46.57 ^c	27.64	48.17	20.53
360	47.95	28.19	49.50	21.31
370	49.45	28.74	50.83	22.09

^a Φ_m^o is $\Phi_m^o = -G_m^o(T) - H_m^o(0)/T = \Delta_0^T S_m^o - \Delta_0^T H_m^o/T$. ^b Extrapolated values. ^c Interpolated values.

The thermodynamic functions for ketol are presented in Table 4. The value of the enthalpy of fusion by adiabatic calorimetry was used in the calculations.

Energy of combustion measurements for ketol are summarized in Table 5. Measurements on samples 4 and 5 compacted in air were made with a terylene ampule. The standard enthalpy of combustion of crystalline ketol

$$\Delta_c H_m^o = -(6963.0 \pm 1.8) \text{ kJ}\cdot\text{mol}^{-1}$$

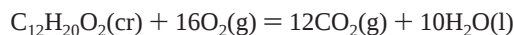
was calculated from the measured energy of combustion

$$\Delta_c U^o = -(6972.9 \pm 1.8) \text{ kJ}\cdot\text{mol}^{-1}$$

using the equation:

$$\Delta_c H^o = \Delta_c U^o + \Delta n RT$$

where Δn is the change of the number of moles of the gaseous products during the reaction under standard conditions:



The molar mass of ketol $M = 196.286 \text{ g}\cdot\text{mol}^{-1}$ was calculated using recommended atomic masses of the elements.¹¹

The standard enthalpy of formation of crystalline ketol

$$\Delta_f H_m^o(\text{cr}, 298.15 \text{ K}) = -(597.6 \pm 2.4) \text{ kJ}\cdot\text{mol}^{-1}$$

was calculated from the standard enthalpy of combustion of ketol and the enthalpies of formation of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$:¹²

$$\Delta_f H_m^o(\text{CO}_2, \text{g}, 298.15 \text{ K}) = -(393.51 \pm 0.13) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^o(\text{H}_2\text{O}, \text{l}, 298.15 \text{ K}) = -(285.83 \pm 0.04) \text{ kJ}\cdot\text{mol}^{-1}$$

The standard enthalpy of formation of liquid ketol

$$\Delta_f H_m^o(\text{ketol}, 298.15 \text{ K}) = -(577.3 \pm 2.4) \text{ kJ}\cdot\text{mol}^{-1}$$

was calculated using the enthalpy of fusion

$$\Delta_{\text{fus}} H_m^o(306.75 \text{ K}) = (20.81 \pm 0.02) \text{ kJ}\cdot\text{mol}^{-1}$$

converted to $T = 298.15 \text{ K}$ with the use of the heat capacities of the crystalline and liquid ketol (eqs 1 and 2):

$$\Delta_{\text{fus}} H_m^o(298.15 \text{ K}) = (20.32 \pm 0.03) \text{ kJ}\cdot\text{mol}^{-1}$$

Condensation Equilibrium of Cyclohexanone. The equilibrium mole fractions of ketol and cyclohexanone in the temperature range (294 to 367) K are summarized in Table 6. Since the number of moles changes during the reaction, it is necessary to calculate the composition of the components (ketol, cyclohexanone, water, and KOH) in the organic phase in order to determine the equilibrium constant of reaction 1. For the calculations, the solubility of water in mixtures of ketol and cyclohexanone was measured by means of visual-polythermic method. The homogenization temperatures and the clouds temperatures were determined by sight at the heating and cooling, respectively, for the three mixtures of ketol and cyclohexanone with water. The average value of the temperatures was recognized as the temperature of saturation of each mixture. The average heating and cooling rate did not exceed $0.5 \text{ K}\cdot\text{min}^{-1}$. Near the saturation temperatures system was maintained during 30 min at each change of temperature for 0.5 K. The results are summarized in Table 7 and shown in Figure 3. The solubility of water as a function of temperature was fitted by the polynomials:

$$x_2(x_1 = 0.0121) = (-1.071 \pm 0.426) + (4.05 \pm 1.28) \cdot 10^{-3} T/\text{K} \quad (5)$$

$$x_2(x_1 = 0.0326) = (-1.056 \pm 0.633) + (3.97 \pm 1.89) \cdot 10^{-3} T/\text{K} \quad (6)$$

$$x_2(x_1 = 0.1346) = (-0.9982 \pm 0.7094) + (3.67 \pm 2.18) \cdot 10^{-3} T/\text{K} \quad (7)$$

where x_1 is the mole fraction of ketol in the parent organic mixture and x_2 is the mole fraction of water in the saturated solution.

These polynomials were used for the calculation of the equilibrium compositions of the organic phase. For the calculation of the values outside the limits of the direct measurements, the solubility of water in mixtures of cyclohexanone and ketol

Table 5. Determination of the Combustion Energy for 2-(1'-Hydroxycyclohexyl)cyclohexanone^a

expt no.	m g	m_{terylene} g	calorimeter	$K \cdot 10^3$ min^{-1}	ΔT K	$q(\text{HNO}_3)$ J	q_{terylene} J	Σq J	$-\Delta_c U^0$ $\text{J} \cdot \text{g}^{-1}$
1	0.54031		A ^b	2.05	1.2899	4.2		7.6	35527.7
2	0.51576		A ^b	2.03	1.2310	3.6		7.1	35519.7
3	0.50816		B ^b	2.12	1.2093	4.2		7.0	35527.2
4	0.34410	0.02872	B ^b	2.02	0.8628	2.4	657.1	4.9	35521.7
5	0.34872	0.02663	B ^b	2.10	0.8704	2.1	609.3	5.0	35515.3
6	0.50776		C	2.14	1.2275	6.3		7.7	35542.0
7	0.32620		C	2.11	0.7880	3.5		4.4	35517.8
8	0.33072		C	2.03	0.7986	2.4		4.7	35508.4
9	0.34655		C	2.14	0.8372	2.4		5.0	35522.4
10	0.35444		C	2.13	0.8566	2.4		5.1	35538.1
$\langle -\Delta_c U^0 \rangle =$									35524.0 ± 9.2

^a m , mass of the sample; m_{terylene} , mass of terylene; $q(\text{HNO}_3)$, correction for nitric acid formation; q_{terylene} , correction for the heat of combustion of terylene; K , cooling constant of the calorimeter; ΔT , corrected temperature rise; Σq , sum of the Washburn corrections; $\Delta_c U^0$, energy of combustion. ^b These results were obtained by Yuri V. Maksimuk. The authors express their thanks to him. Samples 4 and 5 were combusted in terylene ampules.

Table 6. Equilibrium Mole Fractions of 2-(1'-Hydroxycyclohexyl)cyclohexanone (1) and Cyclohexanone (2) in the Liquid Phase^a

T K	parent substance	no. of expts	mole fraction, x_i		
			x_1	x_2	$10^2 \langle x_1 \rangle$
293.6	a	5	13.27 ± 0.09	86.73 ± 0.09	13.46 ± 0.05
	b	4	13.64 ± 0.01	86.36 ± 0.01	
313.2	a	7	6.29 ± 0.02	93.71 ± 0.02	6.29 ± 0.09
	b	5	6.29 ± 0.18	93.71 ± 0.02	
333.2	a	7	3.29 ± 0.05	96.71 ± 0.05	3.26 ± 0.04
	b	10	3.24 ± 0.05	96.76 ± 0.05	
352.9	a	4	1.61 ± 0.03	98.39 ± 0.03	1.60 ± 0.02
	b	5	1.60 ± 0.03	98.40 ± 0.03	
367.4	a	4	1.23 ± 0.05	98.77 ± 0.05	1.21 ± 0.03
	b	3	1.19 ± 0.02	98.81 ± 0.02	

^a Key: a, cyclohexanone and aqueous solution of KOH (5 %). b, solutions of ketol and cyclohexanone with higher mole fractions of ketol than the equilibrium ones and aqueous solution of KOH (5 %). x_1 , mole fraction of ketol measured by gas-liquid chromatography. x_2 , mole fraction of cyclohexanone measured by gas-liquid chromatography.

Table 7. Solubility of Water (3) in the 2-(1'-Hydroxycyclohexyl)cyclohexanone (1) + Cyclohexanone (2) System^a

$10^2 x_1$	x_3	T_1/K	T_2/K	$\langle T \rangle/\text{K}$
1.21	0.249	326.7	326.2	326.4
	0.253	327.3	327.7	327.5
	0.264	329.7	327.7	328.7
	0.284	332.7	332.7	332.7
	0.312	342.4	341.4	341.9
3.26	0.245	328.2	328.2	328.2
	0.260	331.0	331.4	331.2
	0.280	334.7	334.7	334.7
	0.307	344.95	342.2	343.6
13.46	0.082	294.7	295.2	294.9
	0.230	334.0	333.2	333.6
	0.263	346.0	344.1	345.0

^a x_1 , mole fraction of ketol in a parent mixture of ketol and cyclohexanone. x_3 , mole fraction of water in the saturated solution. T_1 , homogenization temperature. T_2 , clouds temperature. $\langle T \rangle$, temperature of saturation.

was extrapolated. It was assumed that content of KOH in organic phase was much less than the uncertainties in the gas-liquid chromatography measurements of concentrations of ketol and cyclohexanone. Therefore, the content of KOH was not taken into account.

For calculation of K_a , the activity coefficients of the components were evaluated by the UNIFAC group contributions scheme using the program unifac.exe¹³ and the next groups:

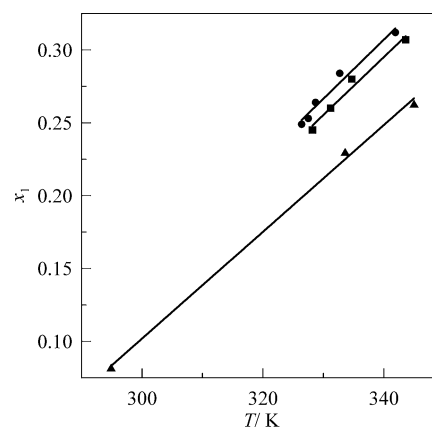


Figure 3. Solubility of water (1) in the cyclohexanone + 2-(1'-hydroxycyclohexyl)cyclohexanone system depending on temperature and mole fraction of ketol (2); x_1 , mole fraction of water in the saturated solution; $x_2 = 0.0121$; $x_2 = 0.0326$; $x_2 = 0.1344$.

ketol: $\text{C}_{12}\text{H}_{20}\text{O}_2 = [8\text{CH}_2, \text{CH}, \text{C}, \text{CH}_2\text{CO}, \text{OH}]$

cyclohexanone: $\text{C}_6\text{H}_{10}\text{O} = [4\text{CH}_2, \text{CH}_2\text{CO}]$

and

water: $[\text{H}_2\text{O}]$

described earlier.¹⁴ The results are summarized in Table 8.

Since the activity coefficients depend on temperature and composition of the mixture, the sum of the components activities (Σa_i) is not constant with the change of temperature. Thus, a normalized equilibrium constant was calculated as

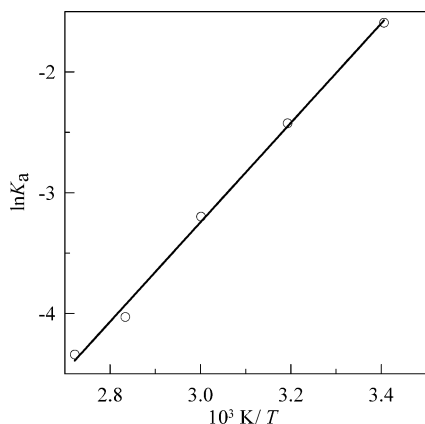
$$K_a(T) = \frac{\left(\frac{a_1}{\sum_i a_i} \right)_T}{\left(\frac{a_2}{\sum_i a_i} \right)_T^2} = \frac{\left(\frac{x_1 \gamma_1}{\sum_i x_i \gamma_i} \right)_T}{\left(\frac{x_2 \gamma_2}{\sum_i x_i \gamma_i} \right)_T^2} \quad (8)$$

where a_1 , x_1 , γ_1 , a_2 , x_2 , and γ_2 are activities, mole fractions, and activity coefficients of ketol and cyclohexanone in an equilibrium mixture, respectively. The equilibrium compositions of the reaction system, the activity coefficients, and the equilibrium constants are presented in Table 8.

Table 8. Equilibrium Contents of the Reacting System 2-(1'-Hydroxycyclohexyl)cyclohexanone (1) + Cyclohexanone (2) + Water (3) in the Liquid Phase^a

T K	10 ² x _i		10 ² x _{i, equil}			γ _i			10 ² a _i			10 ² K _a
	x ₁	x ₂	x ₁	x ₂	x ₃	γ ₁	γ ₂	γ ₃	a ₁	a ₂	a ₃	
293.6	13.46	86.56	12.38	79.71	7.91	0.87	1.05	8.04	10.77	83.70	63.60	24.30
313.2	6.29	93.71	5.18	77.15	17.67	0.74	1.12	6.18	3.83	86.41	109.20	10.23
333.2	3.26	96.74	2.39	70.79	26.83	0.68	1.21	4.77	1.63	85.66	127.98	4.78
352.9	1.60	98.40	1.03	63.40	35.57	0.67	1.35	3.78	0.69	85.59	134.45	2.08
367.4	1.21	98.79	0.71	57.64	41.65	0.71	1.48	3.24	0.50	85.31	134.95	1.52
330.5	$\Delta_{r(1)}H_m^0 = -(34.4 \pm 3.3) \text{ kJ}\cdot\text{mol}^{-1}$											

^a x_i, ratios of the mole fractions of ketol and cyclohexanone (measured by gas–liquid chromatography). x_{i, equil}, mole fractions of ketol, cyclohexanone, and water (calculated with the use of the solubility data). γ_i, activity coefficients of ketol, cyclohexanone, and water. a_i, activities of ketol, cyclohexanone, and water. K_a, equilibrium constants.

**Figure 4.** Temperature dependence of the normalized equilibrium constant $\ln K_a$.

The temperature dependence of the equilibrium constant of reaction 1 was fitted by the polynomial and shown in Figure 4:

$$\ln K_a = (-15.49 \pm 1.22) + (-41.35 \pm 4.00)10^2 \cdot 1/(T/K) \quad (9)$$

The enthalpy of reaction 1 at the average temperature is

$$\Delta_{r(1)}H_m(330.5 \text{ K}) = -(34.4 \pm 3.3) \text{ kJ}\cdot\text{mol}^{-1}$$

The enthalpy of reaction 1 was also calculated at 298.15 K using the calorimetric data:

$$\Delta_f H_m^0(\text{ketol, l, } 298.15 \text{ K}) = -(577.3 \pm 2.4) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^0(\text{cyclohexanone, l, } 298.15 \text{ K}) = -(272.6 \pm 1.8) \text{ kJ}\cdot\text{mol}^{-1} \quad 15$$

$$\Delta_{r(1)}H_m^0(298.15 \text{ K}) = \Delta_f H_m^0(\text{ketol, l, } 298.15 \text{ K}) - 2\Delta_f H_m^0(\text{Chon, l, } 298.15 \text{ K}) = -(32.1 \pm 4.3) \text{ kJ}\cdot\text{mol}^{-1}$$

and was reduced to the average temperature of the measurements:

$$\Delta_{r(1)}H_m^0(330.5 \text{ K}) = -(30.9 \pm 4.4) \text{ kJ}\cdot\text{mol}^{-1}$$

from the temperature dependence of the heat capacities of ketol (Table 4) and cyclohexanone.⁷ This value is in good agreement

with the value $\Delta_{r(1)}H_m^0$, obtained from equilibrium data (Table 8), within the uncertainties of the measurements of both the values.

Conclusions

(1) Enthalpy of formation and entropy of 2-(1'-hydroxycyclohexyl)cyclohexanone were determined by calorimetric investigations. Thermodynamic properties of dimerization of cyclohexanone were calculated.

(2) The equilibrium of dimerization of cyclohexanone was investigated at (294 to 367) K. Thermodynamic properties of the reaction were calculated using the equilibrium constants.

(3) The two values of the enthalpies of dimerization satisfactory fit within their respective uncertainties.

Literature Cited

- (1) Iogansen, A. V.; Kurkchi, G. A.; Baeva, V. P. Aldol condensation of cyclohexanone. *Zh. Org. Khim.* **1971**, 7, 2509–2511 (in Russian).
- (2) Efimova, G. A.; Shutova, I. V.; Shapiro, Yu. E. Autocondensation of cyclohexanone. *Zh. Org. Khim.* **1989**, 25, 1201–1204 (in Russian).
- (3) Kosov, V. I.; Malyshev, V. M.; Milner, G. A.; Sorkin, E. L.; Shibakin, V. F. Multi-purpose set-up for thermophysical measurements controlled with a microcomputer. *Izmer. Tekh.* **1985**, 11, 56–58 (in Russian).
- (4) Kabo, G. J.; Blokhin, A. V.; Kabo, A. G. Investigation of thermodynamic properties of organic substances. *Chem. Probl. Dev. New Mater. Technol.* **2003**, 1, 176–193.
- (5) Pavese, F.; Malyshev, V. M. Routine measurements of specific heat capacity and thermal conductivity of high-Tc superconducting materials in the range 4–300 K using modular equipment. *Adv. Cryog. Eng.* **1994**, 40, 119–124.
- (6) Furukawa, G. T.; McCoskey, R. E.; King, G. J. Calorimetric properties of benzoic acid from 0 to 410 K. *J. Res. Natl. Bureau Stand.* **1951**, 47, 256–261.
- (7) Vasiliev, I. A.; Petrov, V. M. *Thermodynamic Properties of Oxygen-Containing Organic Compounds*; Khimiya: Leningrad, 1984 (in Russian).
- (8) White, G. K.; Collocott, S. J. Heat-capacity of reference materials: Cu and W. *J. Phys. Chem. Ref. Data* **1984**, 13, 1251–1257.
- (9) Kabo, A. G.; Diky, V. V. Details of calibration of a scanning calorimeter of the triple heat bridge type. *Thermochim. Acta* **2000**, 347, 79–84.
- (10) Hubbard, W. N.; Scott, D. W.; Waddington, G. Standard states and corrections for combustions in a bomb at constant volume. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Chapter 5.
- (11) Atomic weights of the elements 2001 (IUPAC Technical Report). *Pure Appl. Chem.* **2003**, 75, 1107–1122.
- (12) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere Publishing Corp.: New York, 1989.
- (13) www.che.udel.edu/thermo/basicprograms.htm#UNIFAC.
- (14) Sandler, S. I. *Chemical and Engineering Thermodynamics*; John Wiley & Sons: New York, 1999.
- (15) Wolf, G. Thermochemical investigation of some cyclic ketones. *Helv. Chim. Acta* **1972**, 55, 1446–1459 (in German).

Received for review March 19, 2005. Accepted September 28, 2005.

JE0501078