THERMODYNAMIC PROPERTIES OF CYCLOPENTANONE AND CYCLOHEXANONE

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The isobaric heat capacities of cyclopentanone and cyclohexanone vapors and their enthalpy of combustion were measured calorimetrically.

This work is a continuation of the study of the properties of cyclic ketones (see [1, 2]), which are required in order to provide the necessary information about the thermophysical data on the starting, intermediate, and final products of their synthesis in designing a number of production processes.

The experimental study of the heat capacity C_p of vapor is carried out on a setup that permits measurements at temperatures of 310-500°K and pressures of 12-110 kPa. The relative error in the determination of C_p does not exceed 0.4%. Precision data on the enthalpy of vaporization ΔH_V can also be obtained at the same time on the setup.

Figure 1 shows a simplified diagram of the calorimetric setup, consisting of a circulation evaporator 1, which is the source for the uniform flow of vapor; a calorimeter 2; a flow-through system, included heated tubes 4, condensers 5 and receptacles 6 for collecting the condensate. The circulation evaporator and calorimeter are placed in oil thermostats 3, whose temperature was maintained to within ±(0.001-0.005)°K.

The evaporator consists of a horizontally positioned glass vessel with a working volume of 130 cm^3, enclosed in a vacuum silver-plated jacket. A 13-Ω electric heater is placed at the bottom of the evaporator. Its heating element consists of Nichrome wire, double-wound on a strip of mica. The element is closed on both sides by thin mica and inserted snugly into a flat copper casing. The casing was chemically nickel-plated and soldered to a Kovar ring, which is soldered hermetically, through junctions, to a glass tube. The protective casing is filled with helium and several layers of platinum wire and wound around it in order to prevent spattering of boiling liquid.

The calorimeter was made from thin-walled purex glass, like the remaining parts of the setup. Standard platinum resistance thermometers without the protective jackets, in order to reduce their thermal inertia, were placed at the inlet and outlet from the calorimeter. A heater is placed at the center of the calorimetric chamber. The 100-Ω heating element was made of Nichrome wire 0.1 mm in diameter, which is placed in the form of a spiral on a mica framework. The current-carrying and potential wires from the heaters H_1 and H_2 and the resistance thermometers are led out through the glass in a hermetically sealed fashion. The calorimetric chamber is surrounded by a vacuum silver-plated envelope.

Before the evaporator was filled with the material under study, the entire system was evacuated and flushed with inert gas. One hundred to 110 ml of the sample were poured into the evaporator through the tap 7, and the system was pressurized to the working level. The presence of a large volume in the setup made it possible to maintain the pressure constant during the experiment. The pressure was measured with an MBP mercury manometer. The thermostats were set to a fixed temperature, the flow-through tubes whose temperature was maintained 20° higher than the boiling temperature of the sample were heated, and the evaporator heater H_1 was switched on. The boiling temperature of the liquid was monitored with a copper–constantan thermocouple T_p.

After this the setup operated for some time in a closed cycle until equilibrium was established. The indications of the calorimeter thermometers T_1 and T_2 were read with a fixed flow rate of vapor F, after which the calorimeter heater H_2 was switched on. The

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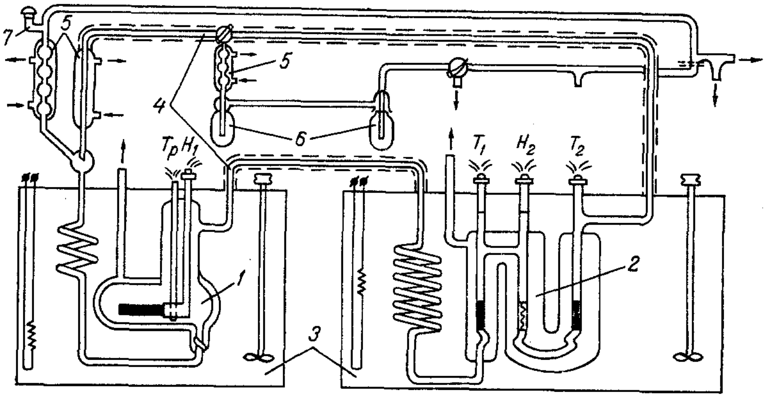

Fig. 1. Diagram of the setup used to determine the heat capacity of vapors by the constant-flow method.

TABLE 1. Experimental Values of the Heat Capacity of Cyclopentanone Vapor C_p

P	T						
	360	375	400	420	440	460	480
101,325				139,49	142,84	146,42	151,81
64,354			132,45	137,18	141,98	145,77	151,39
46,968				136,52	141,00	144,88	150,84
33,578		124,01	130,70	135,82	140,47		150,13
19,459	119,23	122,78	129,45	134,87	140,28	144,59	149,45
16,023	118,82	122,54	128,92				
C_p^0	116,90	121,16	128,03	133,86	139,31	144,04	149,22

temperature rise ΔT_1 and the energy Q_{cal} fed into the calorimeter heater were measured based on the achievement of the stationary operating state of the setup.

Then over a period of 6-10 min we extracted the material, and recorded the time and amount of energy fed into the evaporator heater. The rate of flow of vapor through the calorimeter was determined by weighing the collected condensate. The apparent heat capacity was calculated based on the data obtained:

$$C_p' = \frac{Q_{\text{cal}}}{F(\Delta T_1 \pm \Delta T_2)}. \qquad (1)$$

In many cases the experiments were performed without extracting liquid, and the vapor flow rate was calculated from the known enthalpy of evaporation of the material under study and the energy fed to the evaporator, without taking into account the corrections for the freed volume of liquid in the evaporator. The method used to determine ΔH_V is described in [2].

In order to eliminate possible heat losses in the calorimeter C_p was measured with a constant heater power and different rates of flow of the vapor. The values obtained for the apparent heat capacities depend linearly on the inverse values of the vapor velocity. We determined the true heat capacity by extrapolating the experimental results to infinite velocities.

We checked the operating reliability of the setup by performing measurements for benzene (99.97 mole % pure). The following data on C_p of benzene vapor were obtained: 114.4 J/(mole·K) at T = 403.18°K and P = 36.28 kPa; 115.22 at T = 403.18 and P = 101.325, and 107.3 at T = 373.14 and P = 101.325, which agree well with the published data [3].

The heat capacities of cyclopentanone and cyclohexanone vapors (chromatographic purity higher than 99.9 mole %) were measured in the temperature range 360-480°K every 15-20° for two to five values of the pressure. In each series of measurements (5-11 experiments) the apparent heat capacity values were measured for the corresponding temperature, pressure, and vapor flow rate($(5-14)\cdot 10^{-4}$ mole/sec). The error in determining these quantities is not less than 0.2% for cyclopentanone and 0.3% for cyclohexanone with a probability of 95%. The

TABLE 2. Experimental Values of the Heat Capacity of Cyclohexanone Vapor C_p

P	T					
	385	400	420	440	460	480
101,325				180,01	186,03	192,56
66,846			172,99	179,24	185,20	191,98
42,992		164,57	172,53	177,60	184,82	191,59
31,308		163,98	171,54	177,09	184,68	190,60
18,721	155,84	162,53	169,95	176,21	183,79	
C_p^0	155,20*	161,07	168,98	175,81	183,65	190,18

*Calculated using Eq. (3).

values of C_p for the vapor in the real state were calculated from here taking into account the thermal losses (Tables 1 and 2).

Using the values of the vapor heat capacities in the real state we calculated the coefficients in the linear equations of the dependence $C_p = f(P)$ for each temperature, from which we determined the values of the heat capacities in the ideal gas state $C_p{}^0$. The temperature dependence of $C_p{}^0$ of cyclopentanone is described by the equation

$$C_p^0 = -23{,}775 + 0{,}478964T - 0{,}247184 \cdot 10^{-3}T^2, \qquad (2)$$

and that of cyclohexanone is described by the equation

$$C_p^0 = -44{,}670 + 0{,}63945T - 0{,}31250 \cdot 10^{-3}T^2. \qquad (3)$$

For cyclohexanone the data on C_p agree with the results of [4] within the limits of measurement error. Our values of $C_p{}^0$ for cyclopentanone and cyclohexanone are 7 J/(mole·K) higher than the values computed in [5].

The statistical calculation of the thermodynamic functions [5] carried out based on the molecular and spectral data of [6] took into account the presence of the "bath" form in cyclohexanone differing energetically from the "armchair" form by 23.4 kJ/mole, while for cyclopentanone only the stable form was taken into account. The experimental determination of $C_p{}^0$ of the vapor led to the conclusion that both cyclopentanone and cyclohexanone have intermediate conformational forms which differ energetically from the most stable forms and whose presence must be taken into account in the statistical calculations.

It is reported in [7] that this difference between two intermediate and stable forms equals 11.7 kJ/mole for cyclohexanone. Cyclopentanone also has several conformations; "flat" and "envelope" differ in energy from the most stable "twist" form by 9-10 kJ/mole [8, 9].

The values of $C_p{}^0$ and S_t° were refined taking into account the conformational composition based on the data [5], and the results (see Table 3) agree well with experiment. The vibrational frequencies of cyclopentanone [10], which were employed in [5], differ somewhat from the frequencies selected in [11]. Calculation of $C_p{}^0$ based on these frequencies leads to values of the heat capacity which are too high. The final conclusion regarding the selection of frequencies and the conformational composition can be made after the low-temperature measurements of C_p of cyclopentanone. As regards cyclohexanone, the reliability of our data was checked by a calculation of the ideal gas entropy from the low-temperature measurements [12] of the heat capacity. At T = 298.15°K it equals 335.9 J/(mole·K), which agrees with the data of Table 3.

The heats of combustion of ketones were determined in calorimeters with an isothermal envelope. In this work we employed a self-packing steel bomb designed at Moscow State University. The temperature was measured with a platinum resistance thermometer. The heat value of the calorimeters was determined by burning standard grade K-1 benzoic acid in the bomb. The heat of combustion of benzoic acid under standard conditions was assumed equal −26,434.6 ± 4.5 J/g. The samples were burned (ten experiments) in glass ampuls. A polyethylene film, whose heat of combustion was determined beforehand and equalled −46,350 ± 12 J/g, was used as an auxiliary substance for ignition.

TABLE 3. Heat Capacity and Entropy of Cyclopentanone and Cyclohexanone in the Ideal Gas State

Function	T								
	298,15	300	400	500	600	700	800	900	1000
Cyclopentanone									
C_p^0	93,1	93,6	127,5	155,7	180,0	200,4	217,2	231,2	243,3
S_T^0	315,6	316,1	346,0	376,1	405,7	434,3	461,7	487,8	512,5
Cyclohexanone									
C_p^0	115,9	117,2	159,0	195,0	225,5	250,2	270,7	287,9	302,1
S_T^0	336,4	337,1	375,3	413,3	450,4	486,0	519,9	552,1	582,6

TABLE 4. Enthalpy of Combustion and Formation at 298.15°K

Source	$-\Delta U^0_{com}$ (liq.)	$-\Delta H^0_{com}$ (liq).	$-\Delta H^0_{for}$ (liq.)	ΔH_V	$-\Delta H^0_{for}$ (gas)
Cyclopentanone					
Our data	2869,78±0,74	2873,48±0,74	237,39±0,76	41,63±0,36	195.77±0,78
[13]	2869,68±1,64	2873,52±1,64	237,40±1,66	42,63±0,42	194,77±1,72
[14]	2869,51±0,92	2874,03±0,92	236,48±0,97	42,72±0,30	193,76±0,99
Cyclohexanone					
Our data	3512,87±0,73	3517,81±0,73	272,40±0,74	44,86±0,52	227,54±0,77
[13]	3512,53±1,71	3517,64±1,71	272,64±1,73	44,89±0,63	227,75±1,88
[14]	3513,89±1,05	3518,91±1,05	271,37±1,20	45,06±0,30	226,31±1,22

The results of the measurements (Table 4) performed on two calorimeters agree to within the measurement error. The values of the enthalpy of formation of cyclopentanone and cyclohexanone at 298.15°K were calculated using the values $\Delta H^0_{for\,298}$ (gas) $(CO_2) = -393{,}51 \pm 0{,}13$ kJ/mole and $\Delta H^0_{for\,298}$ (liq) $(H_2O) = -285{,}83 \pm 0{,}04$ kJ/mole.

Our values of the enthalpies of combustion and formation are practically identical to those of [13]. There is a difference only in $\Delta H^0_{for\,298}$(gas) of cyclopentanone, and is attributable to the choice of enthalpies of vaporization. The enthalpies of formation of the ketones studied, presented in [14], differ somewhat, though insignificantly, from our values and those of [13].

NOTATION

C_p, isobaric heat capacity, J/(mole·K); C'_p, apparently isobaric heat capacity, J/(mole·K); ΔH_V, enthalpy of vaporization, kJ/mole; ΔH_{com}, and ΔU_{com}, enthalpy and heat of combustion, kJ/mole; $\Delta H_{for\,298}$, enthalpy of formation at 298.15°K; S_t, entropy, J/(mole·K); T, temperature, °K; P, pressure, kPa; F, vapor flow rate, mole/sec; ΔT_1, temperature rise, °K; ΔT_2, difference in the indications of thermometers T_1 and T_2; T_1 and T_2, platinum resistance thermometers; H_1 and H_2, evaporator and calorimeter heaters; T_p, a thermocouple. The index o denotes values referring to the standard state; (gas) denotes the gaseous state and (liq.) denotes the liquid state.

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PARAMETRIC STUDY OF SPARK BREAKDOWN ACCOMPANYING SUCCESSIVE IGNITION OF DISCHARGE GAPS IN PHOTOPREIONIZATION SCHEMES

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The breakdown and dynamic characteristics of a sectioned spark discharge with successive gap ignition, employed for volume UV preionization, were studied experimentally.

A sectioned spark discharge with successive gap ignition is a simple and effective method of UV preionization for producing volume-uniform discharges at high pressures. Sequential sectioning makes it possible to realize an aperiodic discharge with a steep front and short duration, which provides high uniformity and high intensity of ionization of the medium [1, 2]. The determining factors of the ionizing efficiency of spark discharges are the current strength and the rate of change of the current [3, 4]. In this connection, together with the breakdown and energy characteristics, processes occurring at the formation stage of the discharge and the development dynamics of the discharge are of considerable practical interest.

The purpose of this work is to carry out a parametric investigation of the breakdown and energy characteristics, as well as the dynamics of formation and development of a multispark discharge with sequential sectioning for a wide range of geometric and circuit parameters.

The scheme used to form the discharge is shown in Fig. 1a. Linear chains of spark gaps with a distance of 1 mm between the electrodes and electrodes 0.8 mm in diameter were employed. The scale of sectioning is determined by the sizes of the intermediate capacitors. In the experiments performed the distance between the spark gaps equaled 10 mm, and the distance between the gaps and the reverse current conductor equaled 25 mm. The discharge was created in air at atmospheric pressure. Power was fed to the discharge by means of negative voltage pulses with an approximate 20 nsec leading edge and a characteristic exponential decay time of 4 μsec.

The measurement procedure included oscillographic recording of the current and voltage as well as the scan of the discharge emission with an image convertor tube. The voltage on the charging capacitor and at different points along the discharge chain was determined with the help of ohmic dividers. The discharge current was measured with the help of low-inductance shunts at the beginning and end of the discharge line (I_1 and I_2 in Fig. 1a). The intermediate capacitance, the number of gaps, and the amplitude of the voltage pulse were variable parameters.

It was established experimentally that the process of formation of a multispark breakdown with successive sectioning occurs in three stages. This is illustrated by the typical oscillograms of the current and voltage and scanning of the discharge emission (see Figs. 1b and c). At the first stage, whose duration is $\tau_1 = t_1 - t_0$, sequential breakdown of the gaps, maintained by the charging of the intermediate capacitors C_i, occurs. This stage is

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