Low-Temperature Heat Capacities and Standard Molar Enthalpy of Formation of Potassium Hydrogen Phthalate $C_8H_5KO_4$(s)

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Potassium hydrogen phthalate (KHP) was synthesized by the method of liquid-phase synthesis, in which phthalic acid and potassium hydroxide were chosen as the reactants. The structure and composition of the compound were characterized by chemical and elemental analyses, X-ray powder diffraction, and X-ray crystallography. Low-temperature heat capacities of the compound were measured by a precision automated adiabatic calorimeter over the temperature range from (78 to 400) K. A polynomial equation of the heat capacities as a function of the temperature was fitted by a least-squares method. The smoothed heat capacities and the thermodynamic functions of the compound relative to 298.15 K were calculated and tabulated at an interval of 5 K. In accordance with Hess' law, a thermochemical cycle was designed. The enthalpy change of the reaction of phthalic acid with potassium acetate was determined to be $\Delta_r H_m^o = -(4.298 \pm 0.493)$ $kJ\cdot mol^{-1}$ by use of an isoperibol solution-reaction calorimeter, and the standard molar enthalpy of formation of $C_8H_5KO_4$(s) was calculated to be $\Delta_f H_m^o(C_8H_5KO_4, s) = -(1028.05 \pm 0.61)$ $kJ\cdot mol^{-1}$ by use of the enthalpies of dissolution and other auxiliary thermodynamic quantities.

Introduction

Phthalic acid is an important raw material in organic synthesis, which is applied to make dyestuffs, polyester resins, and polyester in the field of macromolecular or polymeric materials. Potassium hydrogen phthalate (abbreviated as KHP) is a well-known monopotassium salt of phthalic acid that can be widely used as both a standard substance for acid and base titration analysis[1] and a pH standard,[2] which may be attributed to its stability in air, making it easy to weigh accurately and to keep a stable pH in solution. KHP is also able to serve as a buffering agent in combination with HCl or NaOH solution. In addition, it is an important intermediate in the production of more complex phthalates which are vastly spread in various trades including commercial manufacturing, agricultural production, and the food service industry.

In recent years, many reports about the piezo-electric, pyro-electric, elastic, and nonlinear optical properties of KHP have been reported in the literature.[3,4] However, until now, studies about the thermodynamic properties of the compound are few, which restricts the progress of relevant theoretical study and application development. The heat capacity and standard molar enthalpy of formation of a substance are some of the most fundamental thermodynamic properties and are closely related to other physical, biological, physiological, and chemical properties. The standard molar enthalpy of formation of a substance is one of the important pieces of data required when calculating enthalpy changes, equilibrium constants, and theoretical yields of reactions in which the substance is involved. The purpose of the present work is to measure low-temperature heat capacities of the compound by adiabatic calorimetry and determine the dissolution enthalpies of the reactants and the products of a designed thermochemical reaction by isoperibol solution-reaction calorimetry. Moreover, some thermodynamic parameters, such as smoothed heat capacities and the standard molar enthalpy of formation of the product $C_8H_5KO_4$(s), were derived from these experimental results.

Experimental Section

Synthesis and Characterization of KHP $C_8H_5KO_4$(s). Phthalic acid and potassium hydroxide were chosen as the reactants, accurately weighed at the molar ratio of $n(C_8H_6O_4)/n(KOH) = 1{:}1$. First, the appropriate amount of potassium hydroxide was dissolved into some double-deionized water in a three-neck flask with a round bottom. Then, phthalic acid was slowly added into the above solution under sufficient stirring. The transparent solution was boiled and refluxed for 2 h, whereafter the liquid mixture was condensed by boiling off some of the solvent until a crystal membrane emerged from the solution surface. The final solution was naturally cooled to room temperature and filtered, and the filter cake was washed three times using anhydrous ethanol (A.R.); a white product was gained. Then, the product was recrystallized three times with a mixed solution of anhydrous ethanol and double deionized water, and a clean white sample was obtained. Finally, the sample was placed in a vacuum desiccator at the temperature of 50 °C to dry in vacuum for 6 h. Theoretical contents of K, C, H, and O in the compound have been calculated to be (19.14, 47.05, 2.47, and 31.34) %, respectively. Chemical and element analyses (model: PE-2400, Perkin-Elmer, USA) have shown that the practical contents of K, C, H, and O in the compound have been measured to be (19.11, 47.06, 2.46, and 31.37) %, respectively. This showed that the purity of the sample prepared was higher than 0.9959 as a mass fraction.

Whether the new synthesized compound is novel or not can be determined by the X-ray powder diffraction (XRD) technique (model XD-3, Beijing Purkinje General Instrument Co., Ltd.,

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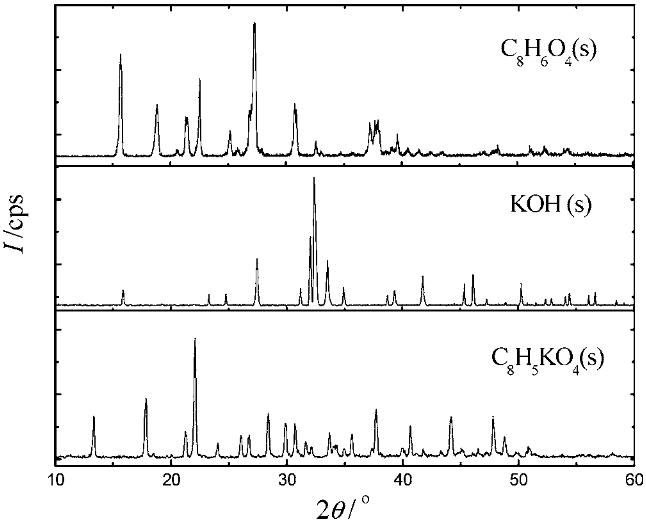

Figure 1. XRD spectra of phthalic acid, potassium hydroxide, and KHP.

China). XRD spectra of phthalic acid, potassium hydroxide and KHP are plotted in Figure 1. The step length of the powder diffraction angle was 0.01°, the wavelength 0.154056 nm (Cu $K\alpha_1$ radiation), the electric voltage 36 kV, and the electric current 20 mA. The scanning rate was 4 $\text{deg}\cdot\text{min}^{-1}$, and a graphite monochromator was used for the filter. It is found from Figure 1 that six obvious absorption peaks are seen at angles of $2\theta = (16, 18, 21, 22, 27, \text{and } 31)$ deg in the diffraction pattern of the phthalic acid. Six obvious absorption peaks were seen at angles of (27.5, 32, 32.5, 33.5, 42, and 46) deg in the chart of potassium hydroxide. Seven distinct characteristic absorption peaks were seen at angles of $2\theta = (13, 18, 22, 28, 38, 44, \text{and } 48)$ deg in the diffractogram of KHP. Therefore, novel characteristic peaks appeared in the diffraction chart of KHP different from those of phthalic acid and potassium hydroxide. It was shown that a new substance was produced by the reaction of phthalic acid with potassium hydroxide. In addition, except for the absorption intensity of several characteristic peaks being a little different, the experimental X-ray diffraction data of KHP is basically consistent with the standard diffractogram of KHP from JCPDS 15-0805. It shows that the purity of the title compound is guaranteed.

A single crystal with dimensions of 0.48 mm × 0.42 mm × 0.30 mm suitable for X-ray analysis was mounted on a fiber. All diffraction data for the compound were collected on a Bruker Smart-1000 CCD area detector diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. The structure was solved by direct methods, expanded using Fourier techniques with the SHELXL-97 program,[5] and refined with a full-matrix least-squares technique on $F.^2$ All non-hydrogen atoms were refined anisotropically. All H-atoms were located theoretically and refined. Absorption corrections were applied by SADABS.

The molecular structure of $C_8H_5KO_4(s)$ is plotted in Figure 2, which is different from that previously reported in the literature.[6] The crystal parameters, data collection, and refinement results for the compound are listed in Table 1. It is found from Table 1 that the crystal system of the compound is orthorhombic, the space group is $Pca2_1$, and the unit cell dimensions are $a = 9.6574(9)$ Å, $b = 13.3821(14)$ Å, $c = 6.5062(7)$ Å, $\alpha = \beta = \gamma = 90°$, and $Z = 4$. All of the bond lengths and angles are listed in Table 2.

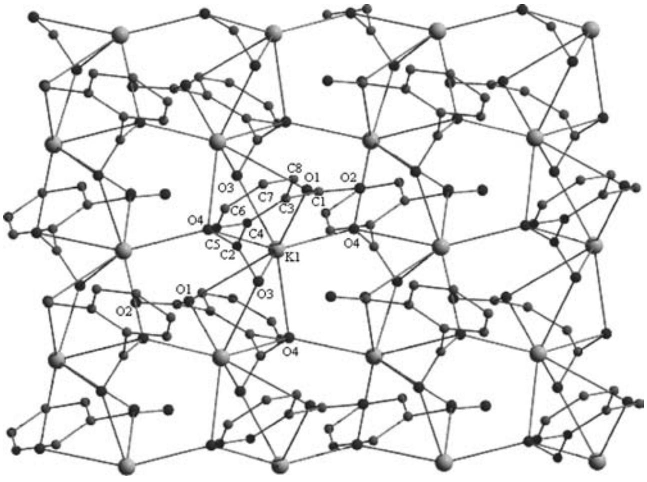

Figure 2. Molecular structure of the title compound $C_8H_5KO_4(s)$.

Table 1. Crystal Data and Structure Refinement for KHP

crystallographic data	structure refinement
empirical formula	$C_8H_5KO_4$
formula weight	204.22
temperature	298(2) K
wavelength	0.71073 Å
crystal system	orthorhombic
space group	$Pca2_1$
unit cell dimensions	$a = 9.6574(9)$ Å, $b = 13.3821(14)$ Å, $c = 6.5062(7)$ Å; $\alpha = \beta = \gamma = 90°$
volume	840.84(15) $Å^3$
Z	4
calculated density	1.613 $\text{Mg}\cdot\text{m}^{-3}$
absorption coefficient	0.607 mm^{-1}
$F(000)$	416
crystal size	(0.48 × 0.42 × 0.30) mm
θ range for data collection	(1.52 to 27.02) deg
limiting indices	$-12 \le h \le 12$, $-17 \le k \le 11$, $-5 \le l \le 8$
reflections collected/unique	3622/1419 [$R(\text{int}) = 0.0378$]
completeness to $\theta = 25.01$	99.3 %
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	1419/1/118
goodness-of-fit on F^2	1.072
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0341$, $wR_2 = 0.0825$
R indices (all data)	$R_1 = 0.0425$, $wR_2 = 0.0881$
largest difference, peak and hole	0.262 and -0.359 $\text{e}\cdot\text{Å}^{-3}$

In this work, four phthalate groups are involved in the coordination to the central potassium ion. Being different from the six-coordinated potassium ion reported in the literature,[6] the potassium ion is surrounded by seven oxygen atoms through the mode of forming strong coordination bonds with K—O: three K—O bonds formed by O_4 have bond lengths of [2.645(2), 2.785(3), and 3.006(2)] Å, two by O_3 with distances of [2.808(2) and 2.831(2)] Å, and another two by O_1 with distances of [2.890(2) and 3.158(2)] Å. It is quite obvious that the atom O_2 from the unionized carboxyl group of one phthalate is not coordinated to the potassium ion but forms a hydrogen bond $O_2—H_2\cdots O_3$ with a bond length of 2.566 Å. The unionized carboxyl group has two distinct C—O bonds, $C_1—O_1$ and $C_1—O_2$, which represent C=O and C—OH, respectively, with bond lengths of [1.227(3) and 1.310(3)] Å. In addition, the benzene ring is a slightly distorted regular hexagon with the average C—C distance of 1.394 Å and a C—C—C angle of 120°, and the deviation of all six actual bond lengths and angles in the benzene ring from the regular values were within standard errors of X-ray crystallography. Accordingly, three types of bonds, including the Coulomb interactions between the potassium ions and the ionized carboxyl group of the hydrogen phthalate, hydrogen bonding ($O_2—H_2\cdots O_3$) between the unionized carboxyl group of one molecule and the ionized carboxyl group

Table 2. All Bond Lengths (Å) and Angles (deg) for KHP

K(1)−O(4)[a]	2.645(2)	O(2)−H(2)	0.8200	C(4)−C(5)	1.403(4)
K(1)−O(4)[b]	2.785(3)	O(3)−C(2)	1.271(4)	C(5)−C(6)	1.382(4)
K(1)−O(3)	2.808(2)	O(3)−K(1)[b]	2.831(2)	C(5)−H(5)	0.9300
K(1)−O(3)[c]	2.831(2)	O(4)−C(2)	1.245(3)	C(6)−C(7)	1.386(5)
K(1)−O(1)	2.890(2)	O(4)−K(1)[d]	2.645(2)	C(6)−H(6)	0.9300
K(1)−O(4)	3.006(2)	O(4)−K(1)[c]	2.785(3)	C(7)−C(8)	1.393(5)
K(1)−O(1)[b]	3.158(2)	C(1)−C(3)	1.509(4)	C(7)−H(7)	0.9300
O(1)−C(1)	1.227(3)	C(2)−C(4)	1.520(4)	C(8)−H(8)	0.9300
O(1)−K(1)[c]	3.158(2)	C(3)−C(4)	1.398(4)		
O(2)−C(1)	1.310(3)	C(3)−C(8)	1.401(4)		
O(4)[a]−K(1)−O(4)[b]	89.75(6)	O(4)−K(1)−O(1)[b]	72.02(6)	C(4)−C(3)−C(8)	119.9(3)
O(4)[a]−K(1)−O(3)	129.65(6)	C(1)−O(1)−K(1)	138.46(19)	C(4)−C(3)−C(1)	119.9(2)
O(4)[b]−K(1)−O(3)	86.90(6)	C(1)−O(1)−K(1)[c]	120.51(19)	C(8)−C(3)−C(1)	120.2(3)
O(4)[a]−K(1)−O(3)[c]	89.83(7)	K(1)−O(1)−K(1)[c]	80.53(5)	C(3)−C(4)−C(5)	118.9(3)
O(4)[b]−K(1)−O(3)[c]	133.23(6)	C(1)−O(2)−H(2)	109.5	C(3)−C(4)−C(2)	123.0(2)
O(3)−K(1)−O(3)[c]	126.89(6)	C(2)−O(3)−K(1)	90.07(16)	C(5)−C(4)−C(2)	118.1(2)
O(4)[a]−K(1)−O(1)	83.09(6)	C(2)−O(3)−K(1)[b]	124.38(16)	C(6)−C(5)−C(4)	120.6(3)
O(4)[b]−K(1)−O(1)	138.05(7)	K(1)−O(3)−K(1)[b]	87.93(5)	C(6)−C(5)−H(5)	119.7
O(3)−K(1)−O(1)	67.34(6)	C(2)−O(4)−K(1)[d]	130.28(18)	C(4)−C(5)−H(5)	119.7
O(3)[c]−K(1)−O(1)	88.19(7)	C(2)−O(4)−K(1)[c]	119.02(19)	C(5)−C(6)−C(7)	120.8(3)
O(4)[a]−K(1)−O(4)	148.05(8)	K(1)[d]−O(4)−K(1)[c]	107.10(7)	C(5)−C(6)−H(6)	119.6
O(4)[b]−K(1)−O(4)	117.98(7)	C(2)−O(4)−K(1)	81.68(15)	C(7)−C(6)−H(6)	119.6
O(3)−K(1)−O(4)	44.90(6)	K(1)[d]−O(4)−K(1)	121.71(7)	C(6)−C(7)−C(8)	119.2(3)
O(3)[c]−K(1)−O(4)	82.37(6)	K(1)[c]−O(4)−K(1)	84.95(6)	C(6)−C(7)−H(7)	120.4
O(1)−K(1)−O(4)	65.80(6)	O(1)−C(1)−O(2)	124.7(3)	C(8)−C(7)−H(7)	120.4
O(4)[a]−K(1)−O(1)[b]	138.48(6)	O(1)−C(1)−C(3)	122.0(3)	C(7)−C(8)−C(3)	120.6(3)
O(4)[b]−K(1)−O(1)[b]	64.91(6)	O(2)−C(1)−C(3)	113.3(2)	C(7)−C(8)−H(8)	119.7
O(3)−K(1)−O(1)[b]	83.51(6)	O(4)−C(2)−O(3)	124.6(3)	C(3)−C(8)−H(8)	119.7
O(3)[c]−K(1)−O(1)[b]	85.73(6)	O(4)−C(2)−C(4)	118.0(3)		
O(1)−K(1)−O(1)[b]	137.82(4)	O(3)−C(2)−C(4)	117.4(2)		

Symmetry transformations used to generate equivalent atoms: [a] $x + 1/2, -y + 1, z$. [b] $-x, -y + 1, z - 1/2$. [c] $-x, -y + 1, z + 1/2$. [d] $x - 1/2, -y + 1, z$.

of the neighboring molecule, and van der Waals forces between the aromatic rings, exist in the crystal to form a two-dimensional network and stabilize the structure.

Adiabatic Calorimetry. A precision automatic adiabatic calorimeter was used to measure heat capacities of the compound over the temperature range of $78 \leq (T/\mathrm{K}) \leq 400$. The calorimeter was established in the Thermochemistry Laboratory in the College of Chemistry and Chemical Engineering, Liaocheng University, China. The principle and structure of the adiabatic calorimeter were described in detail elsewhere.[7,8] Briefly, the calorimeter mainly comprised a sample cell, a platinum resistance thermometer, an electric heater, inner, middle, and outer adiabatic shields, three sets of six-junction chromel−constantan thermopiles installed between the calorimetric cell and the inner shield, between the inner and middle shields, and between the middle and outer shields, respectively, and a high vacuum can. The miniature platinum resistance thermometer (IPRT no. 2, produced by Shanghai Institute of Industrial Automatic Meters, 16 mm in length, 1.6 mm in diameter, and a nominal resistance of 100 Ω) was applied to measure the temperature of the sample. The thermometer was calibrated on the basis of ITS-90 by the Station of Low-Temperature Metrology and Measurements, Academia Sinica. The electrical energy introduced into the sample cell and the equilibrium temperature of the cell after the energy input were automatically recorded by use of a data acquisition/switch unit (model 34970A, Agilent), and processed online by a computer.

To verify the accuracy of the calorimeter, the heat capacities of a reference standard material (α-Al_2O_3) were measured over the temperature range of $78 \leq (T/\mathrm{K}) \leq 400$. The sample mass used was 1.7143 g, which was equivalent to 0.0168 mol based on its molar mass, $M(\mathrm{Al_2O_3}) = 101.9613\ \mathrm{g \cdot mol^{-1}}$. Deviations of the experimental results from those of the smoothed curve lie within ± 0.20 %, while the uncertainty is ± 0.30 %, as compared with the values given by the former National Bureau of Standards[9] over the whole temperature range.

Heat capacity measurements were continuously and automatically carried out by means of the standard method of intermittently heating the sample and alternately measuring the temperature. The heating rate and temperature increments were generally controlled at (0.1 to 0.4) $\mathrm{K \cdot min^{-1}}$ and (1 to 3) K. The heating duration was 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period were always kept within (10^{-3} to 10^{-4}) $\mathrm{K \cdot min^{-1}}$ during the acquisition of all heat-capacity data. The data of heat capacities and corresponding equilibrium temperature have been corrected for heat exchange of the sample cell with its surroundings.[7] The sample mass used for calorimetric measurements was 2.0598 g, which was equivalent to 0.01009 mol in terms of its molar mass, $M = 204.22\ \mathrm{g \cdot mol^{-1}}$.

Isoperibol Solution-Reaction Calorimetry. The isoperibol solution-reaction calorimeter consisted primarily of a precision temperature-controlling system, an electric energy calibration system, a calorimetric body, an electric stirring system, a thermostatic bath made from transparent silicate glass, a precision temperature measuring system, and a data acquisition system. The principle and structure of the calorimeter were described in detail elsewhere.[7,10]

The reliability of the calorimeter was verified previously by measuring the dissolution enthalpy of KCl (calorimetric primary standard) in double-distilled water at $T = 298.15$ K. The mean dissolution enthalpy was (17547 ± 13) $\mathrm{J \cdot mol^{-1}}$ for KCl, which was compared with corresponding published data, (17536 ± 3.4) $\mathrm{J \cdot mol^{-1}}$.[11]

In all dissolution experiments of the sample, 100 mL of 1.0 $\mathrm{mol \cdot L^{-1}}$ NaOH was chosen as the calorimetric solvent for measuring the dissolution enthalpies of the reactants and products at $T = 298.15$ K.

Finally, UV−vis spectra and the data of the refractive indexes were used to confirm if the initial solution was in the same thermodynamic state as that of the reacted solution.

Table 3. Experimental Molar Heat Capacities of KHP ($M = 204.22$ $\mathrm{g \cdot mol^{-1}}$)

T/K	$C_{p,\mathrm{m}}$/$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	T/K	$C_{p,\mathrm{m}}$/$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	T/K	$C_{p,\mathrm{m}}$/$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
78.74	81.22	169.7	142.9	286.0	205.6
81.08	82.76	172.7	144.8	289.1	207.5
83.42	85.00	175.6	146.7	292.0	208.6
85.62	86.29	178.5	148.1	294.9	210.1
88.11	88.06	181.5	150.1	298.0	211.0
90.01	90.07	185.5	152.2	300.8	213.2
92.06	91.25	189.6	154.7	303.9	214.1
94.25	92.66	192.5	156.7	306.8	215.5
96.30	94.19	195.4	158.0	309.7	216.9
98.21	95.73	198.3	160.1	312.5	218.1
100.3	97.26	201.4	161.4	315.6	219.7
102.0	98.56	204.3	163.3	318.4	221.3
104.2	100.1	207.3	164.6	321.3	222.0
105.8	101.4	210.2	166.6	324.4	223.4
107.7	102.7	213.1	168.4	327.3	225.0
109.5	103.7	216.1	169.9	330.4	226.6
111.2	104.9	219.1	171.3	333.4	228.1
113.0	106.1	222.0	173.1	336.4	229.7
114.5	107.5	225.0	174.5	339.3	230.9
116.5	108.7	228.0	176.3	342.4	232.2
118.6	110.0	230.8	177.9	345.3	233.3
120.9	111.6	233.8	179.0	348.4	234.4
122.7	112.7	236.8	181.0	351.3	236.4
126.0	114.9	239.8	182.2	354.2	237.5
128.9	117.3	243.5	184.1	357.2	239.2
131.8	119.3	247.5	186.2	360.1	240.5
134.7	120.8	250.4	188.1	363.0	241.3
137.6	123.2	253.4	189.7	365.9	243.0
140.1	124.6	256.4	190.8	368.9	243.7
143.4	126.5	259.4	192.3	371.8	244.8
146.3	128.8	262.4	193.8	374.9	246.8
149.3	130.3	265.3	195.7	377.9	248.3
152.1	132.0	268.2	196.9	380.9	249.4
155.1	134.0	271.1	198.7	383.9	251.0
158.0	135.9	274.1	200.2	386.9	252.0
161.0	138.0	277.1	201.3	390.0	253.4
163.9	139.4	280.1	203.3	393.0	255.0
166.9	141.1	283.1	204.6	396.0	255.9

Results and Discussion

Low-Temperature Heat Capacities. All experimental results are listed in Table 3 and plotted in Figure 3, showing that the heat capacity curve of the compound smoothly increased with temperature. It was shown that the structure of the compound was stable over the temperature range between $T = (78$ and $400)$ K, and no phase change, association, or thermal decomposition occurred. The 114 experimental points in the temperature region between $T = 78$ K and $T = 400$ K were fitted by a least-squares method and a polynomial equation of the experimental molar heat capacities ($C_{p,\mathrm{m}}$) versus reduced temperature (X), $X = f(T)$, has been obtained:

$$C_{p,\mathrm{m}}/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = 182.015 + 84.350X - 12.415X^2 + 4.248X^3 - 0.334X^4 \quad (1)$$

in which $X = (T - 239)/161$. This equation is valid over the temperature range from (78 to 400) K. The relative deviations of experimental molar heat capacities from the smoothed heat capacities calculated by the polynomial equation were within ± 0.30 % except for several points around the lower and upper temperature limits, as shown in Figure 4. The coefficient of determination R^2 for the fitting equals 0.99998.

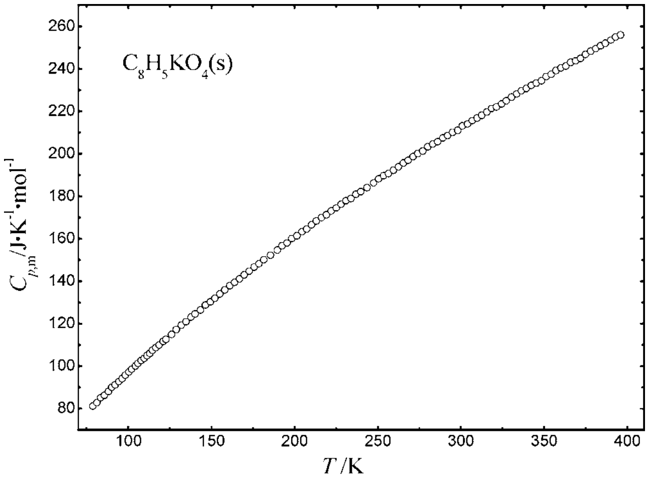

Figure 3. Curve of the experimental molar heat capacities of the compound $C_8H_5KO_4(s)$ versus the temperature (T).

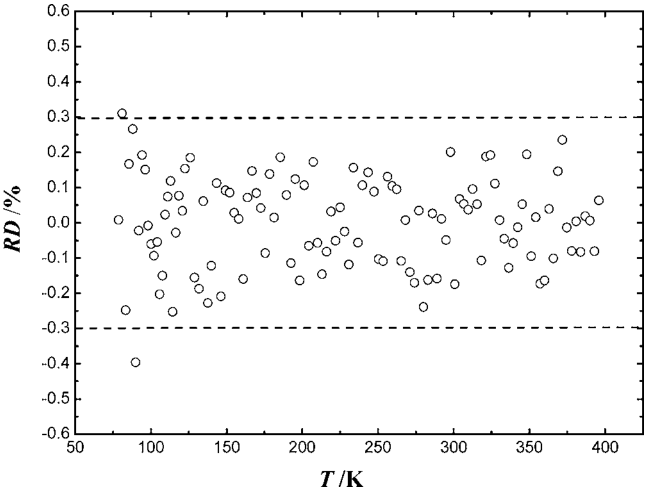

Figure 4. Plot of the relative deviations of the experimental heat capacities (C_{exp}) from the smoothed heat capacities (C_{smo}) of the compound against the absolute temperature, RD/% = $[(C_{\mathrm{smo}} - C_{\mathrm{exp}})/C_{\mathrm{smo}}] \cdot 100$ %.

Thermodynamic Functions of the Compound. The smoothed molar heat capacities and thermodynamic functions of the sample were calculated on the basis of the fitted polynomial of the heat capacity as a function of the reduced temperature (X) according to the following thermodynamic equations:

$$H_{(T)} - H_{(298.15\mathrm{K})} = \int_{298.15\mathrm{K}}^{T} C_{p,\mathrm{m}} \mathrm{d}T \quad (2)$$

$$S_{(T)} - S_{(298.15\mathrm{K})} = \int_{298.15\mathrm{K}}^{T} C_{p,\mathrm{m}} \cdot T^{-1} \mathrm{d}T \quad (3)$$

$$G_{(T)} - G_{(298.15\mathrm{K})} = \int_{298.15\mathrm{K}}^{T} C_{p,\mathrm{m}} \mathrm{d}T - T \int_{298.15\mathrm{K}}^{T} C_{p,\mathrm{m}} \cdot T^{-1} \mathrm{d}T \quad (4)$$

The polynomial fitted values of the molar heat capacities and fundamental thermodynamic functions of the sample relative to the standard reference temperature of 298.15 K are tabulated in Table 4 with an interval of 5 K.

Standard Molar Enthalpy of Formation of KHP $C_8H_5KO_4(s)$. $C_8H_5KO_4(s)$ is supposed to be one of the products in the following liquid-phase reaction,

Table 4. Smoothed Heat Capacities and Thermodynamic Functions of KHP

T	$C_{p,m}$	$H_T - H_{298.15K}$	$S_T - S_{298.15K}$	$G_T - G_{298.15K}$
K	$J \cdot K^{-1} \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$kJ \cdot mol^{-1}$
80	82.19	−33.16	−181.6	−18.63
85	85.98	−32.74	−176.5	−17.73
90	89.71	−32.30	−171.5	−16.86
95	93.39	−31.84	−166.6	−16.02
100	97.02	−31.36	−161.7	−15.20
105	100.6	−30.87	−156.9	−14.40
110	104.1	−30.36	−152.1	−13.63
115	107.6	−29.83	−147.4	−12.88
120	111.1	−29.28	−142.7	−12.16
125	114.5	−28.72	−138.1	−11.46
130	117.8	−28.14	−133.5	−10.78
135	121.1	−27.54	−129.0	−10.12
140	124.4	−26.92	−124.6	−9.486
145	127.7	−26.29	−120.1	−8.875
150	130.8	−25.65	−115.8	−8.285
155	134.0	−24.99	−111.4	−7.716
160	137.1	−24.31	−107.1	−7.110
165	140.2	−23.61	−102.9	−6.644
170	143.2	−22.91	−98.63	−6.140
175	146.2	−22.18	−94.44	−5.656
180	149.2	−21.44	−90.28	−5.193
185	152.2	−20.69	−86.16	−4.751
190	155.1	−19.92	−82.06	−4.330
195	157.9	−19.14	−78.00	−3.929
200	160.8	−18.34	−73.97	−3.548
205	163.6	−17.53	−69.97	−3.188
210	166.4	−16.71	−66.00	−2.847
215	169.2	−15.87	−62.05	−2.526
220	171.9	−15.02	−58.13	−2.226
225	174.6	−14.15	−54.24	−1.944
230	177.3	−13.27	−50.38	−1.683
235	179.9	−12.38	−46.54	−1.441
240	182.5	−11.47	−42.72	−1.218
245	185.1	−10.55	−38.93	−1.014
250	187.7	−9.619	−35.16	−0.8295
255	190.3	−8.674	−31.41	−0.6638
260	192.8	−7.716	−27.69	−0.5169
265	195.3	−6.746	−23.99	−0.3886
270	197.8	−5.763	−20.31	−0.2789
275	200.3	−4.768	−16.66	−0.1875
280	202.8	−3.760	−13.02	−0.1143
285	205.2	−2.740	−9.406	−0.05930
290	207.6	−1.708	−5.813	−0.02224
295	210.0	−0.6640	−2.240	−0.003015
298.15	211.5	0	0	0
300	212.4	0.3922	1.312	−0.001492
305	214.8	1.460	4.845	−0.01754
310	217.1	2.540	8.358	−0.05103
315	219.5	3.632	11.85	−0.1019
320	221.8	4.735	15.33	−0.1699
325	224.1	5.850	18.78	−0.2550
330	226.5	6.977	22.22	−0.3571
335	228.8	8.115	25.64	−0.4761
340	231.0	9.264	29.05	−0.6119
345	233.3	10.43	32.43	−0.7645
350	235.6	11.60	35.80	−0.9338
355	237.8	12.78	39.16	−1.120
360	240.1	13.98	42.49	−1.322
365	242.3	15.18	45.82	−1.542
370	244.6	16.40	49.13	−1.777
375	246.8	17.63	52.42	−2.030
380	249.0	18.87	55.70	−2.299
385	251.2	20.12	58.97	−2.585
390	253.5	21.38	62.23	−2.889
395	255.7	22.65	65.47	−3.209
400	257.9	23.94	68.71	−3.547

$$C_8H_6O_4(s) + CH_3COOK(s) \xrightarrow{\Delta_r H^o_m} C_8H_5KO_4(s) + CH_3COOH(l) \qquad (5)$$

The enthalpy change of reaction 5 can be determined by respective measuring of the enthalpies of dissolution of the $C_8H_6O_4(s)$ and $CH_3COOH(l)$ in 1.0 $mol \cdot L^{-1}$ NaOH solution, $CH_3COOK(s)$ in 1.0 $mol \cdot L^{-1}$ NaOH solution containing a certain amount of the phthalic acid, and $C_8H_5KO_4(s)$ in 1.0 $mol \cdot L^{-1}$ NaOH solution containing a certain amount of acetic acid at 298.15 K.

First, phthalic acid and potassium acetate must be dried in a vacuum desiccator at 50 °C for 4 h. About $1 \cdot 10^{-3}$ mol or 0.166 g of $C_8H_6O_4(s)$ was dissolved in 100 mL of 1.0 $mol \cdot L^{-1}$ NaOH at 298.15 K. If "S" = calorimetric solvent, 1.0 $mol \cdot L^{-1}$ NaOH, then,

$$\{C_8H_6O_4(s)\} + \text{“S”} = \text{solution A}'$$

According to the $n(CH_3COOK)/n(C_8H_6O_4) = 1{:}1$ in reaction 5, about $1 \cdot 10^{-3}$ mol or 0.098 g of $\{CH_3COOK(s)\}$ were dissolved in solution A′, namely,

$$\{CH_3COOK(s)\} + \text{solution A}' = \text{solution A}$$

About $1 \cdot 10^{-3}$ mol or 0.060 g of $\{CH_3COOH(l)\}$ was dissolved in 100 mL of 1.0 $mol \cdot L^{-1}$ NaOH. Because of the easy volatilization of acetic acid, when the liquid was weighed, the temperature in the room must be controlled at (17 to 18) °C to reduce the rate of volatilization, and the sample cell in which the acetic acid was put should be covered with a plug made of the polytetrafluoroethylene. The dissolution enthalpy of $CH_3COOH(l)$ in 1.0 $mol \cdot L^{-1}$ NaOH was measured under the same condition as the above,

$$\{CH_3COOH(l)\} + \text{“S”} = \text{solution B}'$$

The dissolution enthalpy of about $1 \cdot 10^{-3}$ mol or 0.204 g $C_8H_5KO_4(s)$ in a 1.0 $mol \cdot L^{-1}$ NaOH solution containing a certain amount of acetic acid was measured under the same condition as the above,

$$\{C_8H_5KO_4(s)\} + \text{solution B}' = \text{solution B}$$

The measurement results of dissolution enthalpies for the reactants and products of reaction 5 are listed in Table 5.

The enthalpy change of reaction 5 can be calculated in accordance with a thermochemical cycle and the experimental results of the dissolution enthalpy as follows,

$$\begin{aligned}\Delta_r H^o_m &= \sum \Delta_s H^o_{m(\text{reactants})} - \sum \Delta_s H^o_{m(\text{products})} \\ &= \Delta_s H^o_{C_8H_6O_4} + \Delta_s H^o_{CH_3COOK} - (\Delta_s H^o_{CH_3COOH} + \\ &\quad \Delta_s H^o_{C_8H_5KO_4}) \\ &= \Delta H_1 + \Delta H_2 - (\Delta H_3 + \Delta H_4) \\ &= (-75.354) + (-4.790) - [(-53.979) + \\ &\quad (-21.867)] \\ &= -(4.298 \pm 0.493)\ kJ \cdot mol^{-1}\end{aligned}$$

The reaction scheme used to determine the standard molar enthalpy of formation of $C_8H_5KO_4(s)$ is given in Table 6. The experimental values of the dissolution enthalpies of the reactants and products in the liquid-phase reaction 5 were combined with other auxiliary thermodynamic data of $\Delta_f H^o_m(C_8H_6O_4, s) = -782.12\ kJ \cdot mol^{-1}$,[12] $\Delta_f H^o_m(CH_3COOK, s) = -725.15\ kJ \cdot mol^{-1}$,[13] and $\Delta_f H^o_m(CH_3COOH, l) = -(483.52 \pm 0.36)$

Table 5. Dissolution Enthalpies of Reactants and Products of Reaction 5 in the Selected Solvents at $T = 298.15$ K[a]

system	solvent	avg $\Delta_s H_m^o$ kJ·mol^{-1}	no.	m g	$\Delta E_s/\Delta E_e$	t_e s	Q_s J	$\Delta_s H_m^o$ kJ·mol^{-1}
phthalic acid	1.0 mol·L^{-1} NaOH	−75.354 ± 0.060	1	0.16662	1.1969	130.219	−75.744	−75.521
			2	0.16689	1.1508	135.172	−75.595	−75.251
			3	0.16654	1.1567	134.219	−75.445	−75.259
			4	0.16663	1.1541	134.984	−75.706	−75.479
			5	0.16638	1.1508	134.781	−75.373	−75.260
potassium acetate	solution A′	−4.790 ± 0.092	1	0.09830	1.1747	8.921	−5.109	−5.100
			2	0.09823	1.1255	8.781	−4.818	−4.813
			3	0.09833	1.1600	8.531	−4.824	−4.815
			4	0.09810	1.0689	8.953	−4.665	−4.667
			5	0.09779	1.0616	8.766	−4.536	−4.553
acetic acid	1.0 mol·L^{-1} NaOH	−53.979 ± 0.457	1	0.06066	0.8939	123.985	−53.859	−53.317
			2	0.06045	0.9320	123.672	−56.013	−55.642
			3	0.06073	0.9069	123.718	−54.525	−53.914
			4	0.06088	0.9109	123.749	−54.779	−54.032
			5	0.06058	0.8902	123.578	−53.460	−52.992
KHP	solution B′	−21.867 ± 0.149	1	0.20411	0.9779	44.640	−21.280	−21.292
			2	0.20395	1.0047	44.672	−21.879	−21.908
			3	0.20398	1.0126	44.486	−21.959	−21.985
			4	0.20401	1.0107	44.624	−21.987	−22.010
			5	0.20388	1.0222	44.359	−22.104	−22.141

[a] m(g), mass of sample; t_e(s), heating period of electrical calibration; $Q_s = -(\Delta E_s/\Delta E_e)\cdot I^2 R t_e$, heat effect during the sample dissolution; ΔE_s (mV), the voltage change during the sample dissolution; ΔE_e (mV), the voltage change during the electrical calibration; $\Delta_s H_m^o = Q_s/n = -(\Delta E_s/\Delta E_e)\cdot I^2 R t_e (M/m)$, where R is the electro-resistance ($R = 1216.9\ \Omega$ at $T = 298.15$ K), I is the current ($I = 20.015$ mA), and M is molar mass of the sample.

Table 6. Reaction Scheme Used to Determine the Standard Molar Enthalpy of Formation of KHP $C_8H_5KO_4$(s)

no.	reaction	formed solution	$\Delta_f H_m^o$ or $(\Delta_s H_m^o \pm \sigma_a)^a$ kJ·mol^{-1}
1	$\{C_8H_6O_4(s)\}$ + "S" =	A′	−(75.354 ± 0.060), ΔH_1
2	$\{CH_3COOK(s)\}$ + solution A′ =	A	−(4.790 ± 0.092), ΔH_2
3	$\{CH_3COOH(l)\}$ + "S" =	B′	−(53.979 ± 0.457), ΔH_3
4	$\{C_8H_5KO_4(s)\}$ + solution B′ =	B	−(21.867 ± 0.149), ΔH_4
5	$8C(s) + 3H_2(g) + 2O_2(g) = C_8H_6O_4(s)$		−782.12, ΔH_5
6	$2C(s) + 3/2H_2(g) + O_2(g) + K(s) = CH_3COOK(s)$		−725.15, ΔH_6
7	$2C(s) + 2H_2(g) + O_2(g) = CH_3COOH(l)$		−(483.52 ± 0.36), ΔH_7
8	$8C(s) + 5/2H_2(g) + 2O_2(g) + K(s) = C_8H_5KO_4$ (s)		−(1028.05 ± 0.61), ΔH_8

[a] The calorimetric solvent "S" is 1.0 mol·L^{-1} NaOH, $\sigma_a = [(\sum_{i=1}^{5}(x_i - \bar{x})^2)/(n(n-1))]^{1/2}$, in which n is the experimental number; x_i, a single value in a set of dissolution measurements; $\bar{x}$, the mean value of a set of measurement results.

kJ·mol^{-1},[14] to derive the standard molar enthalpy of formation of $C_8H_5KO_4$(s),

$$\begin{aligned}\Delta_f H_m^o(C_8H_5KO_4, s) &= \Delta H_8\\ &= \Delta_r H_m^o + \Delta_f H_m^o(C_8H_6O_4, s) + \Delta_f H_m^o(CH_3COOK, s) - \Delta_f H_m^o(CH_3COOH, l)\\ &= \Delta H_1 + \Delta H_2 - (\Delta H_3 + \Delta H_4) + \Delta H_5 + \Delta H_6 - \Delta H_7\\ &= (-4.298) + (-782.12) + (-725.15) - (-483.52)\\ &= -(1028.05 \pm 0.61)\ \text{kJ·mol}^{-1}\end{aligned}$$

in which $\Delta H_1 \sim \Delta H_8$ were the enthalpy changes of the reactions corresponding to the number of reactions in Table 6.

In this paper, all of the reactants and products of the liquid-phase reaction can be easily dissolved in the corresponding solvents. The results of UV−vis spectra of solution A obtained from the dissolution of the reactants and solution B from the dissolution of the products are shown in Figure 5. The experimental values of the refractive indexes of solution A and solution B were measured to be (1.3421 ± 0.0003) and (1.3419 ± 0.0004), respectively. These results indicate that solution A is consistent with solution B. Therefore, there is no difference in the structure, chemical components, and physicochemical properties between the two solutions.

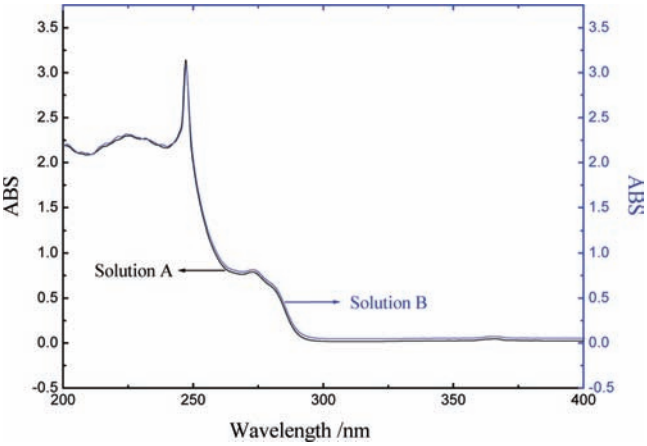

Figure 5. UV−vis spectra of solution A obtained from dissolution of the reactants in the liquid-phase reaction and solution B from dissolution of the products (diluted to 1:20).

Conclusions

The enthalpy change of reaction 5 showed that the designed thermochemical reaction was an exothermic reaction. On the basis of thermodynamic theory, the reaction was an enthalpy-driven process. Moreover, all of the reactants were solid, and the products included one solid and one volatile liquid. It was concluded from an increase of the degree of disorder in the reaction that the entropy change of the reaction was more than zero according to the statistical explanation of the entropy of the system in statistical thermodynamics, and the entropy function of the system was really a measure of “degree of disorder of the system”. Therefore, the reaction should also be an entropy-driven process.

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