Thermodynamics of sodium 5-methylisophthalic acid monohydrate and sodium isophthalic acid hemihydrate

Xin Jin · Zhen Wang · San-Ping Chen · Zhu-Jun Wang · Sheng-Li Gao

Abstract Two crystal samples, sodium 5-methylisophthalic acid monohydrate ($C_9H_6O_4Na_2 \cdot H_2O$, s) and sodium isophthalic acid hemihydrate ($C_8H_4O_4Na_2 \cdot 1/2H_2O$, s), were prepared from water solution. Low-temperature heat capacities of the solid samples for sodium 5-methylisophthalic acid monohydrate ($C_9H_6O_4Na_2 \cdot H_2O$, s) and sodium isophthalic acid hemihydrate ($C_8H_4O_4Na_2 \cdot 1/2H_2O$, s) were measured by a precision automated adiabatic calorimeter over the temperature range from 78 to 379 K. The experimental values of the molar heat capacities in the measured temperature region were fitted to a polynomial equation on molar heat capacities ($C_{p,m}$) with the reduced temperatures (X), $[X = f(T)]$, by a least-squares method. Thermodynamic functions of the compounds ($C_9H_6O_4Na_2 \cdot H_2O$, s) and ($C_8H_4O_4Na_2 \cdot 1/2H_2O$, s) were calculated based on the fitted polynomial equation. The constant-volume energies of combustion of the compounds at $T = 298.15$ K were measured by a precise rotating-bomb combustion calorimeter to be $\Delta_c U(C_9H_6O_4Na_2 \cdot H_2O$, s$) = -15428.49 \pm 4.86$ J g^{-1} and $\Delta_c U(C_8H_4O_4Na_2 \cdot 1/2H_2O$, s$) = -13484.25 \pm 5.56$ J g^{-1}. The standard molar enthalpies of formation of the compounds were calculated to be $\Delta_f H_m^\theta$ ($C_9H_6O_4Na_2 \cdot H_2O$, s) $= -1458.740 \pm 1.668$ kJ mol^{-1} and $\Delta_f H_m^\theta$ ($C_8H_4O_4Na_2 \cdot 1/2H_2O$, s) $= -2078.392 \pm 1.605$ kJ mol^{-1} in accordance with Hess' law. The standard molar enthalpies of solution of the compounds, $\Delta_{sol} H_m^\theta(C_9H_6O_4Na_2 \cdot H_2O$, s) and $\Delta_{sol} H_m^\theta(C_8H_4O_4Na_2 \cdot 1/2H_2O$, s), have been determined as being -11.917 ± 0.055 and -29.078 ± 0.069 kJ mol^{-1} by an RD496-2000 type microcalorimeter. In addition, the standard molar enthalpies of hydrated anion of the compounds were determined as being $\Delta_f H_m^\theta(C_9H_6O_4{}^{2-}$, aq) $= -704.227 \pm 1.674$ kJ mol^{-1} and $\Delta_f H_m^\theta(C_8H_4O_4Na_2{}^{2-}$, aq) $= -1483.955 \pm 1.612$ kJ mol^{-1}, from the standard molar enthalpies of solution and other auxiliary thermodynamic data through a thermochemical cycle.

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Introduction

As an important class of raw material, isophthalic acid derivatives are used to produce paint, polyester resin, unsaturated polyester resin, special fiber, and hot melt adhesives. Recently, with the growth of the study of metal–organic frameworks (MOFs), isophthalic acid derivatives have been extensively employed in the preparation of metal–organic coordination polymers [1–9]. Since isophthalic acid and its derivatives do not dissolve in water, sodium isophthalic acid derivatives are usually employed as reactants in the synthetic process of functional metal–organic coordination. In order to elucidate potential

applications on MOFs involving isophthalic acid derivatives both in theoretically and practically, there is an urgent need for relevant thermodynamic data of sodium isophthalic acid derivatives.

In this article, we synthesized sodium 5-methylisophthalic acid monohydrate ($C_9H_6O_4Na_2 \cdot H_2O$, s) and sodium isophthalic acid hemihydrate ($C_8H_4O_4Na_2 \cdot 1/2H_2O$, s). The low-temperature heat capacities of the title compounds over the temperature range of 78–379 K were measured by an automated adiabatic calorimeter. The standard molar enthalpies of combustion of two compounds at 298.15 K were determined by an RBC-type II type precise rotating-bomb calorimeter. In addition, the standard molar enthalpies of formation of the title compounds were derived from the experimental results.

Experimental section

Chemicals and equipments

5-CH_3-H_2bdc and H_2bdc purchased from the Tokyo Kasti Kogyo Co., Ltd, was of GC grade with a purity of 99%. The gamma aluminum oxide was of spectroscopic pure grade from Shanghai No. 1 Reagent Factory. It was transformed to alpha aluminum oxide in a muffle oven at 1473.15 K before use and maintained in a desiccator with P_4O_{10}. Potassium chloride (mass fraction 0.9999) was purchased from Shanghai No. 1 Reagent Factory, and dried in a vacuum oven at 500 K for 8 h before use. The relative atomic masses used were those recommended by the IUPAC Commission in 1999 [10]. Elemental analyses were performed on an Elemental Vario EL III CHNOS analyzer. TG–DTG were performed on a NETZSCH STA 449C instrument under a dynamic atmosphere of high purity O_2 with a heating rate of 5 °C min^{-1}.

Adiabatic calorimeter

A precision automatic adiabatic calorimeter was used to measure the heat capacities of the compound over the temperature range $78 \leq (T/K) \leq 398$. The principle and structure of the adiabatic calorimeter have been described in detail elsewhere [11–13].

To verify the accuracy of the calorimeter, the heat capacity of the reference standard material (α-Al_2O_3) was measured over the temperature range $78 \leq (T/K) \leq 398$. The sample mass used is 1.7143 g, which is equivalent to 0.0168 mol based on its molar mass, $M(Al_2O_3) = 101.9613$ g mol^{-1}. Deviations of the experimental results from those of the smoothed curve lie within $\pm$ 0.2%, while the uncertainty is $\pm$ 0.3%, as compared with the values given by the former

National Bureau of Standards [14] 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 data of heat capacities and corresponding equilibrium temperature have been corrected for heat exchange of the sample cell with its surroundings [12, 15]. The sample mass used for the calorimetric measurements was 2.8961 g, which is equivalent to 0.0102 mol in terms of its molar mass, $M = 273.107$ g mol^{-1}.

Rotating-bomb combustion calorimeter

The constant-volume combustion energy of the compound was determined by an RBC-type II type precise rotating-bomb combustion calorimeter. The main experimental procedures were described previously [16, 17]. The correct value of the heat exchange was calculated according to the Linio–Pyfengdelel–Wsava formula.

The calorimeter was calibrated with benzoic acid. The calibrated experimental results with an uncertainty of 4.38×10^{-4} are summarized in Table 1. The energy equivalent of the rotating-bomb calorimeter was calculated, and the analytical methods for final products (gas, liquid and solid) were the same as those in Ref. [16]. The results of the IR spectrum and PXRD show that the final solid product is identified hexagonal sodium peroxide. The analyses of the combustion products indicate that the compounds are transformed to CO_2 (g), H_2O (l), N_2 (g), and Na_2O_2 (s) under excess oxygen. The amounts of NO_x and CO in the final gas phase may be neglected. The analytical results of the final products show that the combustion reactions are complete. The energy equivalent of the RBC-type II calorimeter was determined from seven combustion experiments in using approximately 0.8–0.9 g of NIST 39i benzoic acid under experimental conditions to be $\varepsilon_{calor} = 18604.99 \pm 8.14$ J K^{-1}, as indicated in Table S1. Conversion of the energy of the actual bomb process to that of the isothermal process and the correction to standard states were made according to Hubbard et al. [18].

Microcalorimeter

The enthalpy of solution of the complex was measured by an RD496-2000 type microcalorimeter. The main experimental procedures were described previously [17]. The design, assemblage, and test of the microcalorimeter were published in Ref. [19]. The calorimetric constant at 298.15 K was determined by the Joule effect before the experiment, which were 63.901 ± 0.030 μV mW^{-1}. The enthalpy of solution of KCl in deionized water was measured to be 17.581 ± 0.039 kJ mol^{-1}, which is in good

Table 1 Smoothed molar heat capacities and thermodynamic functions of (C$_9$H$_6$O$_4$Na$_2$·H$_2$O, s)

T/K	$C_{p, m}$/J K^{-1} mol^{-1}	$H_T - H_{298.15\ K}$/kJ mol^{-1}	$S_T - S_{298.15\ K}$/J K^{-1} mol^{-1}	$G_T - G_{298.15\ K}$/kJ mol^{-1}
80	185.19	−68.71	−381.6	−38.18
85	193.62	−67.76	−370.1	−36.30
90	201.72	−66.77	−358.8	−34.48
95	209.50	−65.75	−347.7	−32.72
100	216.99	−64.68	−336.8	−31.00
105	224.19	−63.58	−326.0	−29.35
110	231.13	−62.44	−315.4	−27.74
115	237.83	−61.27	−305.0	−26.19
120	244.30	−60.06	−294.8	−24.69
125	250.56	−58.82	−284.7	−23.24
130	256.62	−57.56	−274.7	−21.84
135	262.51	−56.26	−264.9	−20.49
140	268.24	−54.93	−255.3	−19.19
145	273.82	−53.58	−245.8	−17.94
150	279.26	−52.19	−236.4	−16.73
155	284.58	−50.78	−227.1	−15.58
160	289.80	−49.35	−218.0	−14.46
165	294.92	−47.89	−209.0	−13.40
170	299.95	−46.40	−200.1	−12.37
175	304.92	−44.89	−191.4	−11.40
180	309.82	−43.35	−182.7	−10.46
185	314.68	−41.79	−174.1	−9.571
190	319.49	−40.20	−165.7	−8.722
195	324.27	−38.59	−157.3	−7.915
200	329.03	−36.96	−149.0	−7.150
205	333.77	−35.30	−140.9	−6.426
210	338.51	−33.62	−132.8	−5.743
215	343.24	−31.92	−124.7	−5.100
220	347.99	−30.19	−116.8	−4.496
225	352.74	−28.44	−108.9	−3.932
230	357.52	−26.66	−101.1	−3.407
235	362.32	−24.86	−93.37	−2.921
240	367.14	−23.04	−85.69	−2.473
245	372.00	−21.19	−78.07	−2.064
250	376.90	−19.32	−70.51	−1.692
255	381.83	−17.42	−63.00	−1.357
260	386.81	−15.50	−55.54	−1.060
265	391.82	−13.55	−48.13	−0.7999
270	396.88	−11.58	−40.76	−0.5767
275	401.99	−9.585	−33.43	−0.3902
280	407.14	−7.562	−26.15	−0.2402
285	412.34	−5.513	−18.90	−0.1265
290	417.58	−3.438	−11.69	−0.04909
295	422.86	−1.337	−4.507	−0.007697
298.15	426.21	0	0	0
300	428.19	0.7903	2.642	−0.002237
302	430.33	1.649	5.493	−0.01009
310	438.95	5.126	16.85	−0.09864

Table 1 continued

T/K	$C_{p, m}/J K^{-1} mol^{-1}$	$H_T - H_{298.15 K}/kJ mol^{-1}$	$S_T - S_{298.15 K}/J K^{-1} mol^{-1}$	$G_T - G_{298.15 K}/kJ mol^{-1}$
315	444.38	7.334	23.92	−0.2003
320	449.84	9.570	30.96	−0.3374
325	455.32	11.83	37.98	−0.5099
330	460.82	14.12	44.97	−0.7177
335	466.34	16.44	51.94	−0.9606
340	471.86	18.79	58.90	−1.239
345	477.38	21.16	65.83	−1.551
350	482.90	23.56	72.74	−1.899
355	488.40	25.99	79.63	−2.282
360	493.88	28.44	86.51	−2.698
365	499.32	30.93	93.36	−3.150
370	504.73	33.44	100.2	−3.635
375	510.09	35.97	107.0	−4.154

agreement with the value of 17.584 ± 0.007 kJ mol^{-1} in Ref. [20]. The relative error of the experiment result is 0.02% and the RSD of the calorimeter is 0.3%, which indicates that the calorimetric system is accurate and reliable.

Synthesis and characterization

5-CH$_3$-H$_2$bdc and H$_2$bdc were mixed with sodium hydroxide in water at the molar ratio of n(5-CH$_3$-H$_2$bdc or H$_2$bdc): n(NaOH) = 1:2 at 80 °C, respectively. Followed by evaporation and filtration, white crystals were produced. The compounds were identified by elemental analysis as the formula C$_9$H$_8$O$_5$Na$_2$ (Calculated: C, 44.64%; H, 3.33%; O, 33.04%. Found: C, 44.26%; H, 3.61%; O, 33.28%) and C$_8$H$_5$O$_{4.5}$Na$_2$ (Calculated: C, 43.85%; H, 2.30%; O, 32.86%. Found: C, 43.29%; H, 2.72%; O, 32.63%).

The purity of the samples was identified by high performance reversed phase liquid chromatography under isocratic conditions. The column was packed with C$_{18}$ sorbents (150 × 4.6 mm) with particle diameter of 5 μm, the mobile phase contained 20 mmol KH$_2$PO$_4$ in methanol and the pH value was adjusted to 2. Flow rate was 1 mL min^{-1}, and the components were detected at 254–261 nm. Values of normalized area of peaks are 99.69 and 99.76%. Results are demonstrated that the samples have high purity and meet the requirements for thermochemical measurements.

TG–DTG tests of the title compounds were under a dynamic atmosphere of oxygen with a flow rate of 30 cm^3 min^{-1} and a heating rate of 5 K min^{-1}. As shown in Fig. 1, there are three stages of weight loss in the measured temperature range. The first step displays at 149.2–216 °C with the mass loss of 7.52% (the calculated mass loss is 7.44%), which is due to dehydration. The second step shows
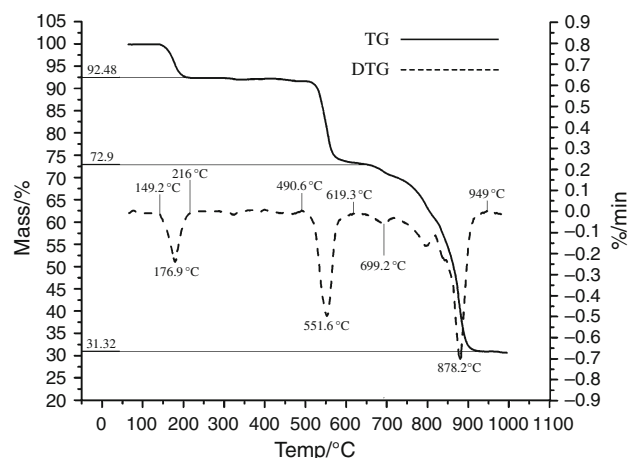

Fig. 1 TG–DTG of C$_9$H$_6$O$_4$Na$_2$·H$_2$O (s)

a sharp mass loss of 19.58% from 490.6 to 619.3 °C. The third step shows an enormous mass loss of 41.58% from 699.2 to 949 °C in which the C$_9$H$_8$O$_5$Na$_2$ is decomposed to Na$_2$O$_2$ confirmed by PXRD. There are three stages of weight loss in the measured temperature range from Fig. 2. The first step illustrates from 93 to 138 °C with the mass loss of 4.02% (the calculated mass loss is 4.11%), which is due to dehydration. The second step shows a mass loss of 30% from 519 to 589 °C. The third step demonstrates a tremendous mass loss of 34.77% from 772 to 921 °C in which the C$_8$H$_5$O$_{4.5}$Na$_2$ is decomposed to Na$_2$O$_2$ confirmed by PXRD.

Results and discussion

Low-temperature heat capacity

All experimental results are listed in Tables S1 and S2 and are plotted in Figs. 3 and 4. Figure 3 shows that the
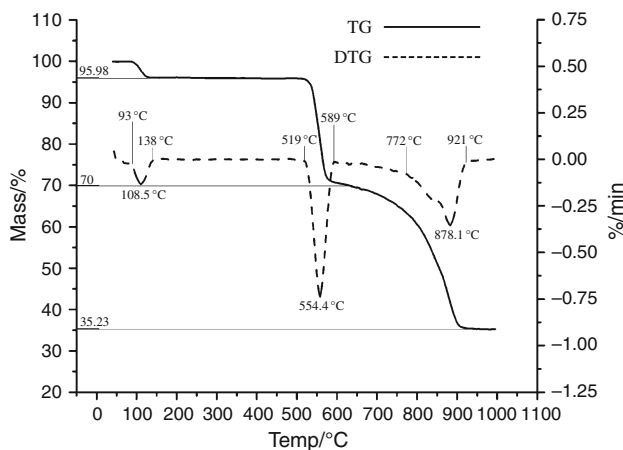
Fig. 2 TG–DTG of $C_8H_4O_4Na_2 \cdot 1/2H_2O$ (s)

Fig. 4 Curve of the experimental molar heat capacities of $(C_8H_4O_4Na_2 \cdot 1/2H_2O, s)$ versus the temperature (T)

$(C_9H_6O_4Na_2 \cdot H_2O, s)$ is stable over the temperature range of 78–378 K, that is, there are no phase change, association, or thermal decomposition occurred. The 99 experimental points in the temperature region of 78–378 K are fitted by means of the least-squares method, and a polynomial equation of the experimental molar heat capacities $[C_{p,m}, (C_9H_6O_4Na_2 \cdot H_2O, s)]$ versus reduced temperature (X), $X = f(T) = [T/K - 1/2(T_1 + T_2)]/[1/2(T_1 - T_2)]$ (where $T_1 = 378$ K and $T_2 = 78$ K), has been obtained.

$$
\begin{aligned}
C_{p,m}/(J\ K^{-1}\ mol^{-1}) =\ & 355.60527 + 143.31748X \\
& + 9.78846X^2 + 22.4612X^3 \\
& - 17.90166X^4
\end{aligned} \tag{1}
$$

In which $X = T - 228/150$. This equation is valid between 78 and 378 K.

The coefficient of determination for the fitting R^2 equals 0.99999.

Figure 4 shows that the $(C_8H_4O_4Na_2 \cdot 1/2H_2O, s)$ is stable over the temperature range of 78–379 K, that is, no
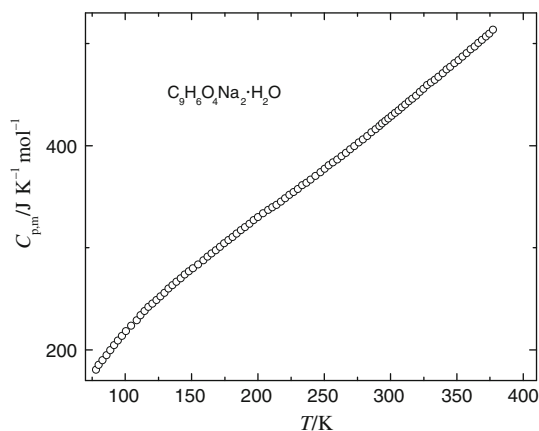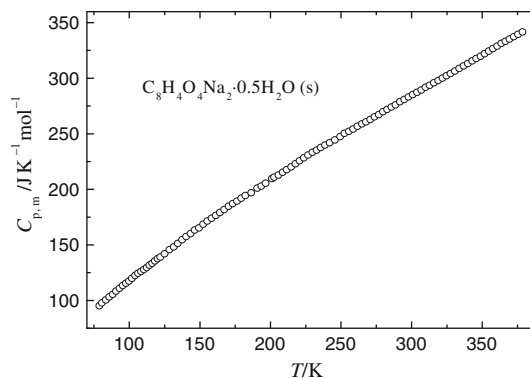
phase change, association, or thermal decomposition occurred. The 105 experimental points in the temperature region of 78–379 K are fitted by means of the least-squares method, and a polynomial equation of the experimental molar heat capacities $[C_{p,m}, (C_8H_4O_4Na_2 \cdot 1/2H_2O, s)]$ versus reduced temperature (X), $X = f(T) = [T/K - 1/2(T_1 + T_2)]/[1/2(T_1 - T_2)]$ (where $T_1 = 379$ K and $T_2 = 78$ K) has been obtained.

$$
\begin{aligned}
C_{p,m}/(J\ K^{-1}\ mol^{-1}) =\ & 231.58556 + 116.42611X \\
& - 14.51269X^2 + 7.53003X^3 \\
& + 1.53868X^4
\end{aligned} \tag{2}
$$

In which $X = T - 228.5/150.5$. This equation is valid between 78 and 379 K. The coefficient of determination for the fitting R^2 equals 0.99997.

The thermodynamic functions

The smoothed molar heat capacities and thermodynamic functions were calculated based on the fitted polynomial of the heat capacities as a function of the reduced temperature (X) according to the following thermodynamic equations

$$(H_T - H_{298.15}) = \int_{298.15}^{T} C_p dT \tag{3}$$

$$(S_T - S_{298.15}) = \int_{298.15}^{T} C_p T^{-1} dT \tag{4}$$

$$(G_T - G_{298.15}) = \int_{298.15}^{T} C_p dT - T \int_{298.15}^{T} C_p T^{-1} dT \tag{5}$$

The polynomial fitted values of the molar heat capacities and fundamental thermodynamic functions of the samples relative to the standard reference temperature 298.15 K are tabulated in Tables 1 and 2 at 5 K intervals.

The constant-volume energy of combustion and the standard molar enthalpy of combustion.

Fig. 3 Curve of the experimental molar heat capacities of $(C_9H_6O_4Na_2 \cdot H_2O, s)$ versus the temperature (T)

Table 2 Smoothed molar heat capacities and thermodynamic functions of ($C_8H_4O_4Na_2\cdot1/2H_2O$, s)

T/K	$C_{p, m}$/J K^{-1} mol^{-1}	$H_T - H_{298.15\ K}$/kJ mol^{-1}	$S_T - S_{298.15\ K}$/J K^{-1} mol^{-1}	$G_T - G_{298.15\ K}$/kJ mol^{-1}
80	96.802	−42.88	−232.1	−24.31
85	102.12	−42.39	−226.1	−23.17
90	107.39	−41.86	−220.1	−22.05
95	112.59	−41.31	−214.2	−20.97
100	117.73	−40.74	−208.3	−19.91
105	122.81	−40.14	−202.4	−18.88
110	127.83	−39.51	−196.6	−17.89
115	132.80	−38.86	−190.8	−16.92
120	137.70	−38.18	−185.0	−15.98
125	142.55	−37.48	−179.3	−15.07
130	147.34	−36.76	−173.6	−14.18
135	152.08	−36.01	−168.0	−13.33
140	156.76	−35.24	−162.4	−12.50
145	161.38	−34.44	−156.8	−11.71
150	165.96	−33.62	−151.2	−10.93
155	170.48	−32.78	−145.7	−10.19
160	174.94	−31.92	−140.3	−9.476
165	179.36	−31.03	−134.8	−8.788
170	183.73	−30.12	−129.4	−8.126
175	188.05	−29.19	−124.0	−7.492
180	192.32	−28.24	−118.7	−6.885
185	196.55	−27.27	−113.3	−6.304
190	200.73	−26.28	−108.0	−5.750
195	204.87	−25.26	−102.8	−5.222
200	208.97	−24.23	−97.54	−4.721
205	213.02	−23.17	−92.34	−4.245
210	217.04	−22.10	−87.16	−3.796
215	221.02	−21.00	−82.01	−3.372
220	224.96	−19.89	−76.88	−2.974
225	228.87	−18.75	−71.79	−2.602
230	232.74	−17.60	−66.72	−2.255
235	236.59	−16.43	−61.67	−1.934
240	240.40	−15.23	−56.65	−1.637
245	244.19	−14.02	−51.66	−1.366
250	247.94	−12.79	−46.69	−1.120
255	251.68	−11.54	−41.75	−0.8981
260	255.39	−10.28	−36.82	−0.7012
265	259.08	−8.989	−31.93	−0.5290
270	262.75	−7.685	−27.05	−0.3812
275	266.41	−6.362	−22.20	−0.2577
280	270.05	−5.021	−17.36	−0.1584
285	273.68	−3.661	−12.55	−0.08330
290	277.30	−2.284	−7.765	−0.03215
295	280.90	−0.8884	−2.995	−0.004891
298.15	283.18	0	0	0
300	284.51	0.5252	1.755	−0.001408
302	285.95	1.096	3.650	−0.006650
310	291.71	3.406	11.20	−0.06538

Table 2 continued

T/K	$C_{p, m}$/J K^{-1} mol^{-1}	$H_T - H_{298.15 K}$/kJ mol^{-1}	$S_T - S_{298.15 K}$/J K^{-1} mol^{-1}	$G_T - G_{298.15 K}$/kJ mol^{-1}
315	295.31	4.874	15.89	−0.1326
320	298.91	6.359	20.57	−0.2233
325	302.52	7.863	25.23	−0.3372
330	306.13	9.384	29.88	−0.4744
335	309.76	10.92	34.50	−0.6347
340	313.40	12.48	39.12	−0.8181
345	317.06	14.06	43.72	−1.024
350	320.73	15.65	48.30	−1.254
355	324.43	17.27	52.88	−1.506
360	328.15	18.90	57.44	−1.781
365	331.90	20.55	61.99	−2.079
370	335.68	22.22	66.53	−2.399
375	339.49	23.90	71.06	−2.743

Table 3 Experimental results for the combustion energy of the (C$_9$H$_6$O$_4$Na$_2$·H$_2$O, s) (mol. wt 242.136)

No	1	2	3	4	5	6
m/g	0.97295	1.11130	1.00655	1.05905	1.11670	1.10455
ΔT_{test}/K	0.7962	0.9101	0.8232	0.8672	0.9148	0.9055
ζ/K	0.0122	0.0138	0.0127	0.0131	0.0138	0.0136
ΔT/K	0.8084	0.9239	0.8359	0.8803	0.9286	0.9191
W/J K^{-1}	18604.99	18604.99	18604.99	18604.99	18604.99	18604.99
G/J cm^{-1}	0.9	0.9	0.9	0.9	0.9	0.9
b/cm	12.6	12.6	12.6	12.6	12.6	12.6
ΔU_{Σ}/J	23.08	25.93	23.55	25.01	26.32	25.86
$-\Delta_c U$/J g^{-1}	15418.36	15431.48	15412.91	15427.38	15434.55	15446.25
$-\Delta_c U_{mean}$/J g^{-1}	15428.49 ± 4.86					

Table 4 Experimental results for the combustion energy of the (C$_8$H$_4$O$_4$Na$_2$·1/2H$_2$O, s) (mol. wt 219.102)

No	1	2	3	4	5	6
m/g	1.25505	1.26750	1.25460	1.25385	1.26060	1.25895
ΔT_{test}/K	0.9014	0.9093	0.9005	0.8988	0.9062	0.9028
ζ/K	0.0108	0.0109	0.0108	0.0108	0.0108	0.0108
ΔT/K	0.9122	0.9202	0.9113	0.9096	0.9170	0.9136
W/J K^{-1}	18604.99	18604.99	18604.99	18604.99	18604.99	18604.99
G/J cm^{-1}	0.9	0.9	0.9	0.9	0.9	0.9
b/cm	12.6	12.6	12.6	12.6	12.6	12.6
ΔU_{Σ}/J	32.87	33.16	32.78	32.82	33.03	32.99
$-\Delta_c U$/J g^{-1}	13493.80	13479.96	13479.96	13468.32	13505.12	13473.00
$-\Delta_c U_{mean}$/J g^{-1}	13484.25 ± 5.56					

ΔU_{Σ} is the standard state correction; $\Delta_c U_{mean}$ is mean value of the combustion energy

The method for determining the constant-volume energies of combustion of the compounds was the same as that used in the calibration of the combustion calorimeter with benzoic acid [21]. The measured results for the constant-volume energies, $\Delta_c U$/J g^{-1}, of combustion of the compounds are given in Tables 3 and 4.

The standard molar enthalpies of combustion of (C$_9$H$_6$O$_4$Na$_2$·H$_2$O, s) and (C$_8$H$_4$O$_4$Na$_2$·1/2H$_2$O, s) refer to
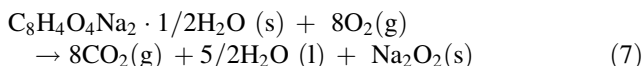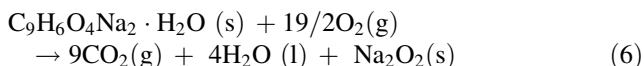
Table 5 Experimental data of $\Delta_{sol}H_m^\theta(C_9H_6O_4Na_2 \cdot H_2O, s)$ at 298.15 K

Run.	Q/mJ	$\Delta_{sol}H_m^\theta$/kJ mol^{-1}	$W(H_2O)$/g	$W(C_8O_6NH_3Na_2 \cdot H_2O)$/g
1	−896.7	−11.936	9.00023	0.01819
2	−873.3	−11.866	9.00063	0.01782
3	−889.7	−11.889	9.00049	0.01812
4	−883.7	−11.921	9.00072	0.01795
5	−896.3	−12.151	9.00057	0.01786
6	−880.7	−11.736	9.00066	0.01817
Mean ± SD	−11.917 ± 0.055			

Table 6 Experimental data of $\Delta_{sol}H_m^\theta(C_8H_4O_4Na_2 \cdot 1/2H_2O, s)$ at 298.15 K

Run.	Q/mJ	$\Delta_{sol}H_m^\theta$/kJ mol^{-1}	$W(H_2O)$/g	$W(C_8O_6NH_3Na_2 \cdot H_2O)$/g
1	−2257.2	−29.023	9.00034	0.01704
2	−2271.1	−28.925	9.00041	0.01687
3	−2260.7	−29.257	9.00054	0.01693
4	−2289.7	−29.269	9.00038	0.01714
5	−2216.2	−28.869	9.00026	0.01682
6	−2317.1	−29.127	9.00081	0.01743
Mean ± SD	−29.078 ± 0.069			

the enthalpy changes of reaction (6) and (7) at 298.15 K and 100 kPa.

$$C_9H_6O_4Na_2 \cdot H_2O \ (s) + 19/2O_2(g)$$
$$\rightarrow 9CO_2(g) + 4H_2O \ (l) + Na_2O_2(s) \quad (6)$$

$$C_8H_4O_4Na_2 \cdot 1/2H_2O \ (s) + 8O_2(g)$$
$$\rightarrow 8CO_2(g) + 5/2H_2O \ (l) + Na_2O_2(s) \quad (7)$$

The standard molar enthalpies of combustion of the title compounds can be derived from the constant-volume energies of combustion by Eq. 8.

$$\Delta_c H_m^\theta = \Delta_c U + \Delta n R T \quad (8)$$

where Δn is the total amount (in mole) of the gases present as products or reactants. $R = 8.314$ J K^{-1} mol^{-1}, $T = 298.15$ K. $\Delta_c H_m^\theta(C_9H_6O_4Na_2 \cdot H_2O, s)$ and $\Delta_c H_m^\theta(C_8H_4O_4Na_2 \cdot 1/2H_2O, s)$ are calculated to be −3737.04 ± 1.18 and −2954.42 ± 1.22 kJ mol^{-1}.

The standard molar enthalpy of formation

The standard molar enthalpies of formation of the compounds are calculated by Hess's law according to Eqs. 9 and 10:
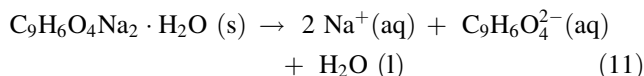
$$\Delta_f H_m^\theta(C_9H_6O_4Na_2H_2O, s)$$
$$= 9\Delta_f H_m^\theta(CO_2, g)$$
$$\quad + 4\Delta_f H_m^\theta(H_2O, l)$$
$$\quad + \Delta_f H_m^\theta(Na_2O_2, s) - \Delta_c H_m^\theta(C_9H_6O_4Na_2H_2O, s) \quad (9)$$

$$\Delta_f H_m^\theta(C_8H_4O_4Na_2 \cdot 1/2H_2O, s)$$
$$= 8\Delta_f H_m^\theta(CO_2, g) + 5/2\Delta_f H_m^\theta(H_2O, l)$$
$$\quad + \Delta_f H_m^\theta(Na_2O_2, s) - \Delta_c H_m^\theta(C_8H_4O_4Na_2 \cdot 1/2H_2O, s) \quad (10)$$

In Eqs. 9 and 10, the standard molar enthalpies of formation of CO$_2$ (g), H$_2$O (l), and Na$_2$O$_2$ (s) recommended by Refs. [22, 23]. $\Delta_f H_m^\theta(CO_2, g) = -393.51 \pm 0.13$ kJ mol^{-1}, $\Delta_f H_m^\theta(H_2O, l) = -285.830 \pm 0.042$ kJ mol^{-1}, and $\Delta_f H_m^\theta(Na_2O_2, s) = -510.87 \pm 0.014$ kJ mol^{-1} are employed in the calculation of $\Delta_f H_m^\theta(C_9H_6O_4Na_2 \cdot H_2O, s)$ and $\Delta_f H_m^\theta(C_8H_4O_4Na_2 \cdot 1/2H_2O, s)$. The standard molar enthalpies of formation of the title compounds can be derived to be $\Delta_f H_m^\theta(C_9H_6O_4Na_2 \cdot H_2O, s) = -1458.74 \pm 1.67$ kJ mol^{-1} and $\Delta_f H_m^\theta(C_8H_4O_4Na_2 \cdot 1/2H_2O, s) = -2078.39 \pm 1.61$ kJ mol^{-1}.

The standard molar enthalpy of solution and the standard molar enthalpy of the hydration anion.

$\Delta_{sol}H_m^\theta(C_9H_6O_4Na_2 \cdot H_2O, s) = -11.917 \pm 0.055$ kJ mol^{-1} and $\Delta_{sol}H_m^\theta(C_8H_4O_4Na_2 \cdot 1/2H_2O, s) = -29.078 \pm 0.069$ kJ mol^{-1}, in H$_2$O, at 298.15 K are given in Tables 5 and 6. The standard enthalpies of hydration anions of the title compounds can be calculated by Hess's law according to Eqs. 11 and 12.

$$C_9H_6O_4Na_2 \cdot H_2O \ (s) \rightarrow 2\ Na^+(aq) + C_9H_6O_4^{2-}(aq)$$
$$+ H_2O \ (l) \quad (11)$$

$$C_8H_4O_4Na_2 \cdot 1/2H_2O \text{ (s)} \rightarrow 2\,Na^+(aq) + C_8H_4O_4^{2-}(aq)$$
$$+ 1/2\,H_2O(l) \qquad (12)$$
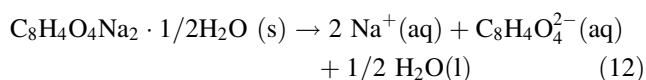
The standard molar enthalpies of the hydration anions of the title compounds are calculated by Eqs. 13 and 14.

$$\Delta_f H_m^\theta(C_9H_6O_4^{2-}, \text{ aq}) = \Delta_{sol}H_m^\theta(C_9H_6O_4Na_2 \cdot H_2O, \text{ s})$$
$$+ \Delta_f H_m^\theta(C_9H_6O_4Na_2 \cdot H_2O, \text{ s})$$
$$- 2\Delta_f H_m^\theta(Na^+, \text{ aq}) - \Delta_f H_m^\theta(H_2O, \text{ l})$$
$$(13)$$

$$\Delta_f H_m^\theta(C_8H_4O_4^{2-}, \text{ aq}) = \Delta_{sol}H_m^\theta(C_8H_4O_4Na_2 \cdot 1/2H_2O, \text{ s})$$
$$+ \Delta_f H_m^\theta(C_8H_4O_4Na_2 \cdot 1/2H_2O, \text{ s})$$
$$- 2\Delta_f H_m^\theta(Na^+, \text{ aq}) - 1/2\Delta_f H_m^\theta$$
$$(H_2O, \text{ l})$$
$$(14)$$

$\Delta_f H_m^\theta(C_9H_6O_4^{2-}, \text{ aq})$ and $\Delta_f H_m^\theta(C_8H_4O_4^{2-}, \text{ aq})$ are calculated to be -704.227 ± 1.674 and -1483.955 ± 1.612 kJ mol^{-1}, where the value of $\Delta_f H_m^\theta(Na^+, \text{ aq})$ is from Ref. [22].

Conclusions

The molar heat capacities of sodium 5-methylisophthalic acid monohydrate and sodium isophthalic acid hemihydrate were measured over the temperature range from 78 to 379 K by a high-precision automated adiabatic calorimeter. The constant-volume combustion energy of the title compounds, $\Delta_c U(C_9H_6O_4Na_2 \cdot H_2O, \text{ s})$ and $\Delta_c U(C_8H_4O_4Na_2 \cdot 1/2H_2O, \text{ s})$, have been determined as being -15428.49 ± 4.86 J g^{-1} and -13484.25 ± 5.56 J g^{-1} by an RBC-II precision rotating-bomb combustion calorimeter at 298.15 K. The standard molar enthalpies of solution of the title compounds, $\Delta_{sol}H_m^\theta(C_9H_6O_4Na_2 \cdot H_2O, \text{ s})$ and $\Delta_{sol}H_m^\theta(C_8H_4O_4Na_2 \cdot 1/2H_2O, \text{ s})$, have been determined as being -11.917 ± 0.055 and -29.078 ± 0.069 kJ mol^{-1} by an RD496-2000 type microcalorimeter. The standard molar enthalpies of combustion, $\Delta_c H_m^\theta(C_9H_6O_4Na_2 \cdot H_2O, \text{ s})$ and $\Delta_c H_m^\theta(C_8H_4O_4Na_2 \cdot 1/2H_2O, \text{ s})$, the standard molar enthalpies of formation, $\Delta_f H_m^\theta(C_9H_6O_4Na_2 \cdot H_2O, \text{ s})$ and $\Delta_f H_m^\theta(C_8H_4O_4Na_2 \cdot 1/2H_2O, \text{ s})$, the standard molar enthalpies of hydration anions of the title compounds, $\Delta_f H_m^\theta(C_9H_6O_4^{2-}, \text{ aq})$ and $\Delta_f H_m^\theta(C_8H_4O_4^{2-}, \text{ aq})$, have been calculated to be $-3737.04 \pm 1.18, -2954.42 \pm 1.22, -1458.740 \pm 1.668, -2078.392 \pm 1.605, -704.227 \pm 1.674,$ and -1483.955 ± 1.612 kJ mol^{-1}, respectively.

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