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STANDARD ENTHALPY OF FORMATION OF PLATINUM HYDROUS OXIDE[*]

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Abstract

Standard enthalpies of formation of amorphous platinum hydrous oxide $PtH_{2.76}O_{3.89}$ (Adams' catalyst) and dehydrated oxide $PtO_{2.52}$ at T=298.15 K were determined to be –519.6±1.0 and –101.3 ±5.2 kJ mol^{-1}, respectively, by micro-combustion calorimetry. Standard enthalpy of formation of anhydrous PtO_2 was estimated to be –80 kJ mol^{-1} based on the calorimetry. A meaningful linear relationship was found between the pseudo-atomization enthalpies of platinum oxides and the coordination number of oxygen surrounding platinum. This relationship indicates that the Pt–O bond dissociation energy is 246 kJ mol^{-1} at T=298.15 K which is surprisingly independent of both the coordination number and the valence of platinum atom. This may provide an energetic reason why platinum hydrous oxide is non-stoichiometric.

Keywords: micro-combustion calorimetry, platinum hydrous oxide, standard enthalpy of formation

Introduction

Various oxides of platinum are found in literature [1–3]. These materials have been widely used as catalyst not only in research laboratories but also in automobiles [4]. Electrochemical application of the hydrous oxides has been made in chemical industry [4]. Some of the oxides are known to be mixed valent [3]. Thus, platinum oxides have been very interesting materials to chemists. However, thermochemical properties of these materials have not been established yet. Recently, the author successfully determined the standard enthalpy of formation of platinic acid ($H_2Pt(OH)_6$) in the crystalline state [5] by using the technique of micro-combustion calorimetry [6]. In fact, this is the first confirmed thermochemical quantity of platinum hydroxides. The present paper reports combustion calorimetry, DSC, and TG on three kinds of platinum hydrous oxides. The results are discussed from the viewpoint of Pt–O dissociation energy.

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Experimental

Materials

Anhydrous platinum oxides are partly decomposed under atmospheric pressure and not easy to handle under the air [3]. Pure stoichiometric anhydrous oxides may not be obtainable. So, the author examined the hydrous oxides in the present study. $PtO_2 \cdot xH_2O$ (Adams' catalyst 99.99%, sample A) and $PtO_2 \cdot H_2O$ (99.9%, sample C) were purchased from Aldrich and used without further purification. The composition of sample A was determined to be $PtH_{2.76}O_{3.89}$ by analyzing the gas emitted thermally under oxygen gas flow and weighing the platinum metal after the thermal decomposition. Obviously, this is not exactly a hydrated dioxide $PtO_2 \cdot xH_2O$, because it includes excess amount of oxygen by 0.5 mole. X-ray diffraction pattern of sample A shows just a broad peak at 35° of 2θ (CuK_α), indicating amorphous. Sample A was dehydrated by being heated to 723 K at the rate of 10 K min^{-1} under nitrogen gas flow. This dehydrated sample (sample B) was determined to be $PtO_{2.52}$ by mass reduction.

Combustion calorimetry

Sample A and B of ca 3 mg were enclosed in an envelope made of platinum foil (0.01 mm in thickness). The envelope was fixed above a pellet of benzoic acid (NIST SRM 39i, 1.6 mm in diameter, ca 5 mg) on the platinum boat (Fig. 1). The sample and benzoic acid were precisely weighed by using ultra-microbalance (Sartorius, 4504MP8). The platinum boat was fixed in the combustion bomb, in which oxygen gas was charged to 4.1 MPa. Fire was ignited by discharging electric current to platinum wire (0.03 mm in diameter) which contacted to benzoic acid. Oxygen in the bomb was humidified by water of 10 mm^3. The average of the energy equivalent of the calorimeter and the standard deviation of the mean were determined to be 67.8395±0.0039 J K^{-1} by burning benzoic acid (six experiments). The details of calorimeter have been presented elsewhere [6]. Samples were thermally decomposed to Pt(*cr*), $H_2O(l)$, and $O_2(g)$ by burning benzoic acid. The complete reaction was confirmed by weighing the residual platinum metal on the boat after calorimetry. The energy of the decomposition was determined from the loss of combustion energy [5].

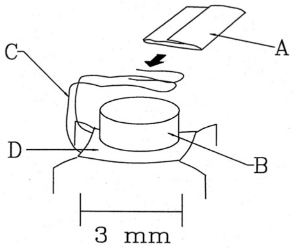

Fig. 1 Sample arrangement for micro-combustion calorimetry. A – a platinum foil enclosing sample; B – a pellet of benzoic acid (ca 5 mg); C – a platinum support; D – a platinum boat

Thermal analysis

DSC and TG of sample A and C were carried out by using Perkin Elmer DSC7 and TGA7 under high-purity oxygen gas flow at the heating rate of 10 K min^{-1}, respectively. Temperature of DSC was calibrated with the melting of In at T=429.8 K and Zn at T=692.8 K. Temperature of TG was calibrated with the magnetic transitions of alumel at T=436 K and Fe at T=1053 K.

Results

Combustion calorimetry

Table 1 lists the auxiliary quantities used in calculation. Tables 2 and 3 summarize the results of combustion calorimetry of sample A and B, respectively. The standard enthalpies of isothermal decomposition reaction at p=0.1 MPa and T=298.15 K were determined as follows.

$$\text{Sample A: } PtH_{2.76}O_{3.89}=Pt(cr)+1.38H_2O(l)+1.26O_2(g), \quad (1)$$

$$\Delta_r H°=125.2\pm1.0 \text{ kJ mol}^{-1}$$

$$\text{Sample B: } PtO_{2.52}=Pt(cr)+1.26O_2(g), \quad (2)$$

$$\Delta_r H° =101.3\pm5.2 \text{ kJ mol}^{-1}$$

$$\text{Platinic acid: } H_2Pt(OH)_6(cr)=Pt(cr)+4H_2O(l)+O_2(g), \quad (3)$$

$$\Delta_r H°=144.6\pm3.6 \text{ kJ mol}^{-1} \text{ [5].}$$

Uncertainty is twice the overall standard deviation of the mean. By using $\Delta_f H°(H_2O, l)= -285.830\pm0.0042$ kJ mol^{-1} [7], the standard enthalpies of formation of sample A and B were derived to be –519.6±1.0 and –101.3±5.2 kJ mol^{-1}, respectively.

Table 1 Auxiliary quantities for the calculation of standard energies of decomposition reaction[a]

Materials	Formula	ρ/g cm^{-3}	M/g mol^{-1}	c_p/J g^{-1} K^{-1}	$(\partial u/\partial p)_T$/ J g^{-1} MPa^{-1}
Sample A	$PtH_{2.76}O_{3.89}$	(6.31)	260.100	(0.494)	(–0.053)
Sample B	$PtO_{2.52}$	(7.00)	235.400	(0.318)	(–0.053)
Benzoic acid	$C_7H_6O_2$	1.32[b]	122.123	1.21[c]	(–0.053)
Petroleum jelly	$CH_{1.953}$[d]	0.9[d]	13.979	(2.21)	(–0.293)

[a] ρ, density; M, molar mass; c_p, heat capacity; $(\partial u/\partial p)_T$, energy of compression. Values in parentheses are estimated. [b] Certificate of analysis (NIST SRM 39i);[c] [10]; [d] [11]

Table 2 Summary of combustion calorimetry of sample A ($PtH_{2.76}O_{3.89}$)[a]

Expt. No.	1	2	3	4
m (sample A)/mg	2.7319	4.9433	6.5771	2.9809
m (BA)/mg	4.9535	4.8475	4.9831	4.8307
m (Vas)/mg	0.0440	0.0549	0.0626	0.0530
m (Pt)/mg	2.0487(2.0489)	3.7057(3.7074)	4.9676(4.9328)	2.1992(2.2357)
n (HNO_3)/μmol	0.084	0.076	0.083	0.062
ε^{i}/J K^{-1}	0.439	0.441	0.443	0.442
ε^{f}/J K^{-1}	0.445	0.447	0.450	0.448
T_i/°C	23.61213	23.61246	23.61142	23.61258
T_f/°C	25.550294	25.508479	25.549056	25.515927
ΔT_c/K	0.008540	0.014378	0.010328	0.016629
ΔT_{ad}/K	1.92963	1.88164	1.92730	1.88672
U_{ign}/J	0.046	0.085	0.073	0.061
$-\Delta_{IBP}U$/J	131.710	128.397	131.532	128.769
$\Delta U(HNO_3)$/J	0.005	0.005	0.005	0.004
ΔU_{Σ}/J	0.118	0.121	0.129	0.118
$\Delta_r u°$/J g^{-1}	469.9	466.0	473.3	468.2
$\Delta_r U°$/kJ mol^{-1}	122.2	121.2	123.1	121.8

$<\Delta_r u°>=469.4\pm4.0$ J g^{-1} [b]

$<\Delta_r U°>=122.1\pm1.0$ kJ mol^{-1} [b]

[a] m (sample A), mass of sample A; m (BA), mass of benzoic acid; m (Vas), mass of petroleum jelly; m (Pt), mass of platinum residual and (expected); n (HNO_3), amount of HNO_3; ε^{i}, energy equivalent of the bomb contents in the initial state; ε^{f}, energy equivalent of the bomb contents in the final state; T_i, initial temperature of the reaction period; T_f, final temperature of the reaction period, ΔT_c, correction to temperature rise; ΔT_{ad}, adiabatic temperature rise; U_{ign}, ignition energy; $\Delta_{IBP}U$, energy of isothermal bomb process; ΔU (HNO_3), decomposition energy of HNO_3; ΔU_{Σ}, the correction to standard state; $\Delta_r u°$, standard massic energy of reaction (1); $\Delta_r U°$, standard molar energy of reaction (1)

[b] The uncertainty is twice the overall standard deviation of the mean

Thermal analysis

Figure 2 shows TG and DSC curves of sample A. Abrupt emission of oxygen was observed at T=868 K both in DSC and TG. The magnitude of mass reduction confirmed the result of the elemental analysis. The endothermic signal after oxygen emission may be instrumental, because it was observed that the baseline shifted by the same amplitude as the endothermic signal after the heating scan of sample A. The emission of water makes two endothermic peaks at T=420 and T=580 K, which are similar to those of sample C (Fig. 3). DSC can not precisely determine the enthalpy of the thermal decomposition at T=298.15 K, because of the ambiguity of the baseline and uncertain temperature of the emitted gas. TG of sample C showed oxygen emission at

Table 3 Summary of combustion calorimetry of sample B ($PtO_{2.52}$)[a]

Expt. No.	1	2	3	4
m (sample B)/mg	3.0913[b]	4.6058[c]	2.4024[c]	2.1188[b]
m (BA)/mg	4.8535	5.0040	4.9623	4.8427
m (Vas)/mg	0.0535	0.0550	0.0312	0.0485
m (Pt)/mg	2.5548(2.5617)	3.8169	1.9909	1.7593(1.7559)
n (HNO_3)/μmol	0.048	0.055	0.052	0.059
ε^i/J K^{-1}	0.444	0.441	0.446	0.442
ε^f/J K^{-1}	0.450	0.446	0.452	0.447
T_i/°C	23.61093	23.61257	23.61152	23.61188
T_f/°C	25.523495	25.568188	25.555486	25.522941
ΔT_c/K	0.014551	0.009323	0.012298	0.015697
ΔT_{ad}/K	1.89802	1.94629	1.93167	1.89537
U_{ign}/J	0.061	0.088	0.219	0.056
$-\Delta_{IBP}U$/J	129.545	132.808	131.689	129.364
$\Delta U(HNO_3)$/J	0.003	0.003	0.003	0.004
ΔU_Σ/J	0.118	0.126	0.121	0.118
$\Delta_r u^\circ$/J g^{-1}	402.8	441.8	395.5	428.2
$\Delta_r U^\circ$/kJ mol^{-1}	94.8	104.0	93.1	100.8
	$<\Delta_r u^\circ>=417\pm22$ J g^{-1} [d]			
	$<\Delta_r U^\circ>=98.2\pm5.2$ kJ mol^{-1} [d]			

[a] m (sample B), mass of sample B; $\Delta_r u^\circ$, standard massic energy of reaction (2); $\Delta_r U^\circ$, standard molar energy of reaction (2); the other symbols are similar to those in Table 2.;
[b] m(sample B)=m(sample A)·235.4/260.1.; [c] m(sample B)=m(Pt)·235.4/195.08.; [d] The uncertainty is twice the overall standard deviation of the mean

T=900 K and another gas emission at T=1000 K. The latter may be attributed to the decomposition of platinum bronze $M_xPt_3O_4$, where M is impurity metal [8]. The amount of oxygen emission at T=900 K was 0.8 mole. It should be remarked that the composition of sample C is different from that of sample A.

Discussion

Estimation of $\Delta_f H^\circ(PtO_2$, *solid)*

Supposing $\Delta_f H^\circ(PtO_2$, *solid*$)= -\Delta_r H^\circ(PtO_{2.52})/1.26$, $\Delta_f H^\circ(PtO_2$, *cr*) is derived to be –80.4 kJ mol^{-1} at T=298.15 K. DSC peak area at T=868 K, 71 kJ mol $(O_2)^{-1}$ (an average of 4 experiments) of sample A, is consistent with $\Delta_r H^\circ(PtO_{2.52})$ determined by combustion calorimetry. DSC peak area at T=900 K of sample C was 70 kJ mol $(O_2)^{-1}$. In the previous DSC study of platinic acid, the enthalpy of the O_2 emission at T=875 K was derived to be

86 kJ mol $(O_2)^{-1}$ [5]. Thus, the DSC values are around 80 kJ mol $(O_2)^{-1}$, not strongly depending on the composition of PtO_x. Therefore, $\Delta_f H°(PtO_2$, solid) is estimated to be –80 kJ mol^{-1}. Table 4 summarizes standard enthalpies of formation of platinum oxides and hydroxides.

Table 4 Standard enthalpies of formation of platinum oxides and hydroxides at 298.15 K

Materials	$-\Delta_f H°$(solid)/kJ mol^{-1}
$PtH_{2.76}O_{3.89}$	519.6±1.0[a]
$PtO_{2.52}$	101.3±5.2[a]
PtO_2	80[b]
$H_2Pt(OH)_6$	1287.9±3.6[c]
Pt_3O_4	163[d]
$Pt(OH)_2$	351.9[d]

[a]The present study ; [b]Estimated in the present study ; [c][5]; [d][12]

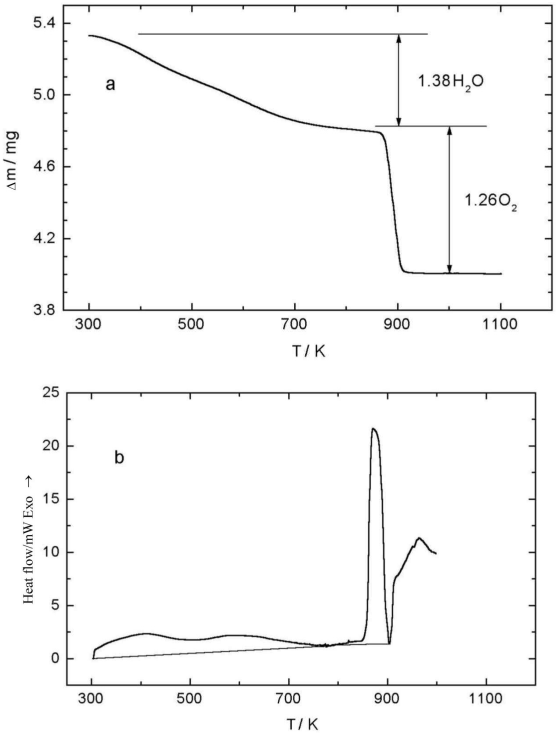

Fig. 2 TG curve (a) and DSC curves (b) of sample A – at a heating rate of 10 K min^{-1} under oxygen gas flow. Sample A of 10.77 mg was loaded on a platinum pan in DSC

Table 5 Enthalpies of pseudo-atomization reaction of platinum oxides and hydroxides

Materials	Reactions	$\Delta_r H°$/kJ mol^{-1}	$\Delta_r H°/\Delta H°$(Pt–O)[a]	Coordination number (Pt–O distance/nm)
$PtH_{2.76}O_{3.89}$	$PtH_{2.76}O_{3.89}$=Pt(*g*)+2.76OH(*g*)+1.13O(*g*)	1474	6.0	6.1 (0.205)[b]
$PtO_{2.52}$	$PtO_{2.52}$=Pt(*g*)+2.52O(*g*)	1294	5.3	
PtO_2	PtO_2=Pt(*g*)+2O(*g*)	1143	4.6	4.5 (0.205)[c] 4.0 (0.192)[d] 2.0 (0.202)[d]
$H_2Pt(OH)_6$	$H_2Pt(OH)_6$=4OH(*g*)+2H_2O(*g*)	1525		
	contribution of H-bond in the crystal	–50[e]		
		1475	6.0	6.0 (0.200)[f]
Pt_3O_4	$PtO_{1.33}$=Pt(*g*)+1.33O(*g*)	952	3.9	4.0 (0.198)[g]
$Pt(OH)_2$	$Pt(OH)_2$=Pt(*g*)+2OH(*g*)	995	4.0	4.0 (0.202)[h]

[a] Supposed the dissociation energy of Pt–O bond $\Delta H°$ (Pt–O)=246 kJ mol^{-1}; [b] Adams' catalyst, [13]; [c] β-PtO_2, [13]; [d] β-PtO_2, [3]; [e] Estimated; [f] [14]; [g] [15]; [h] PtO, [16]

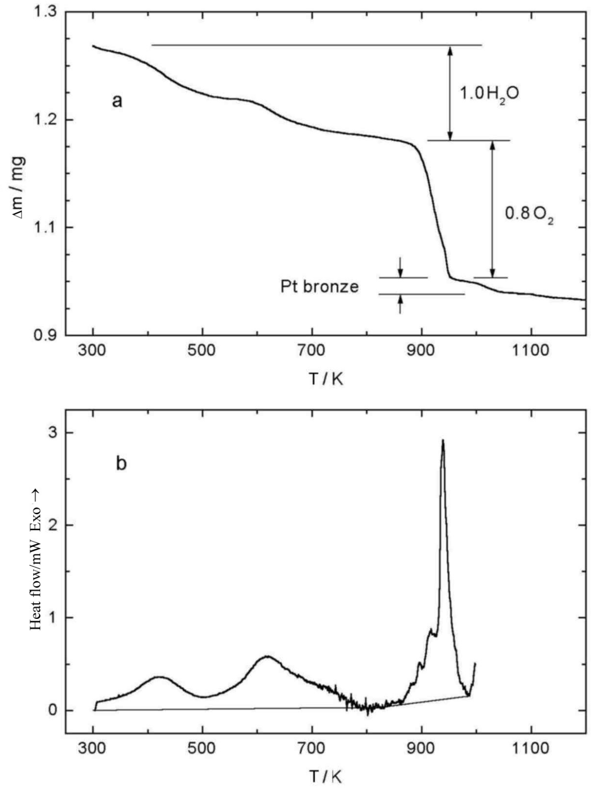

Fig. 3 TG (a) and DSC (b) curves of sample C at a heating rate of 10 K min^{-1} under oxygen gas flow. Sample C of 2.04 mg was loaded on a platinum pan in DSC. Decomposition of Pt bronze was observed at 1000 K

Enthalpies of pseudo-atomization of platinum oxides and hydroxides

Let us assume that all the oxygen atoms form a bond to platinum atom in the platinum oxides, so that platinum atoms are coordinated with O and OH in the hydrous oxide. The isothermal pseudo-atomization reaction at T=298.15 K is defined to be

$$PtH_xO_y(solid)=Pt(g)+xOH(g)+(y-x)O(g) \text{ for } x\leq y$$

and

$$PtH_xO_y(solid)= Pt(g)+(2y-x)OH(g)+(x-y)H_2O(g) \text{ for } x>y.$$

Table 5 summarizes the pseudo-atomization enthalpies $\Delta_{pa}H°$ of platinum oxides and hydroxides accompanied with the coordination numbers in the forth column, which were determined by X-ray crystallography and EXAFS. Standard enthalpies of formation of Pt(g), O(g), OH(g) and $H_2O(g)$ are 565, 249.2±0.1, 39.0±1.2 and 241.83 kJ mol^{-1}, respectively [9]. Hydrogen bond is formed in the $H_2Pt(OH)_6$ crystal. Two hydrogen bonds of 25 kJ mol^{-1} are assumed for a molar $H_2Pt(OH)_6$.

The third column shows the coordination numbers which were calculated by $\Delta_{pa}H°/\Delta H°$(Pt–O), where the bond dissociation energy of Pt–O, $\Delta H°$(Pt–O), was derived to be 246 kJ mol^{-1}. An excellent agreement is found between the calorimetric coordination numbers $\Delta_{pa}H°/\Delta H°$(Pt–O) and the crystallographic and EXAFS coordination numbers.

Conclusions

A meaningful linear relationship was found between the pseudo-atomization enthalpy and the coordination number in platinum oxides and hydroxides. $\Delta H°$(Pt–O) is derived to 246 kJ mol^{-1} at T=298.15 K, which is surprisingly independent of both the coordination number and the valence of platinum atom. This may provide an energetic reason why platinum hydrous oxide is nonstoichiometric.

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