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Enthalpies of formation and DSC and TG results of heteropoly acids containing tungsten and molybdenum

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Abstract

The enthalpies of formation of $H_3PW_{12}O_{40}\cdot 25.0H_2O$ and $H_3PW_{12}O_{40}\cdot 20.0H_2O$ (HPW), $H_4SiW_{12}O_{40}\cdot 6.0H_2O$ (HSiW), $H_3PMo_{12}O_{40}\cdot 8.6H_2O$ (HPMo), and $H_4SiMo_{12}O_{40}\cdot 12.0H_2O$ (HSiMo) have been determined as -18.58, -17.20, -13.14, -12.72 and -13.92×10^3 kJ mol^{-1}, respectively. The formation enthalpies of the anhydrous heteropoly acids have been derived and estimated. The estimated data are -11.36, -11.39, -10.23, and -10.44×10^3 kJ mol^{-1} for $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, and $H_4SiMo_{12}O_{40}$, respectively. The data are in good accordance with that calculated from the formation enthalpies of WO_3, MoO_3, H_3PO_4, and H_4SiO_4. The differential scanning calorimeter (DSC) curve of the hydrated heteropoly acids covers two endothermic and one exothermic peaks. In the light of the temperature at which the Keggin unit collapses and the temperature of the second endothermic peak, the order of the thermal stability should be HPW > HSiW > HPMo > HSiMo. Thermogravimeter (TG) results verify the general formula of hydrated heteropoly acids as $[(1.5H_2O \text{ or } 2H_2O)\cdot(0.5P_2O_5 \text{ or } SiO_2)\cdot 12MO_3\cdot 6H_2O]\cdot xH_2O$, where M=W or Mo, x depends on the species and the condition of preparation of an acid. © 1997 Elsevier Science B.V.

Keywords: Enthalpy of formation; Heteropoly acid; Thermogravimeter; Thermal stability; Tungstophosphoric acid

1. Introduction

Compared with the increasing interest in their effectively catalytic applications, there has been little reported on the thermal behavior of heteropoly acids. The etherification of diethylene glycol with ethanol on HPW, HSiW, and HPMo was reported by Qi et al. [1]. Southward et al. [2] reported the application of HPW and its salts in the high-pressure catalytic oligomerization of propene. Andrushkevich et al. [3] reported the catalytic properties of the thermal decomposition products of HPMo in oxidation of acrolein to acrylic acid. There is, however, no general consensus on the thermal stability of the heteropoly acids [1–4]. In order to promote the application of the heteropoly acids, the knowledge of the thermal behavior and their thermodynamic data are useful and essential.

In previous papers, the enthalpy of formation and thermogravimeter–differential thermal analysis (TG–DSC) curves of HPW [5], and the formation enthalpy, evolved gas detection and infrared analysis of HSiW [6] were reported.

This paper presents the data of formation enthalpy, and DSC and TG results of HPW, HSiW, HPMo, and

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HSiMo. These four heteropoly acids were synthesized and analyzed. The thermodynamic cycles designed for calculating $\Delta_f H_m^o$ of tungsto- and molybdo-heteropoly acids were similar to those for tungstophosphoric acid [5].

The results indicated that, the position of the endo- and exothermic peak of DSC curve and of the weight loss of TG curve implied the difference of the thermal stability of the heteropoly acids; the total water content in a heteropoly acid depended on the species and the condition of preparation; however, six molecules of 'combined' water per Keggin unit in these four acids were identified by TG at the second weight-loss step.

2. Experimental

2.1. Chemicals

Hydrated heteropoly acids were synthesized according to the methods of Booth [7] and Ding [8]. All heteropoly acids obtained were recrystallized twice, heated at 70°C for 2 h, kept in a silica gel-desiccator at 25°C for 14 days until the content of water had become constant, and then analyzed.

Tungsten, phosphorus and silicon were analyzed gravimetrically as reported in previous papers [5,6]. Molybdenum was weighed as molybdic oxide after precipitating as α-benzoinoxime complex and igniting at 510°C.

2.2. DSC and TG

TG and DSC measurements were carried out with Du Pont 1090 thermogravimeter and CDR-1 differential scanning calorimeter, respectively, both in dynamic nitrogen atmosphere and at a heating rate of 10°C min^{-1}.

Temperatures of TG were recorded to 0.1°C. The thermobalance gave results with a precision of 0.01 mg. The presented results of water loss in Table 1 were mean values of three determinations.

The CDR-1 differential scanning calorimeter was a product of the Shanghai Balance Instrument Factory. It gave a precision of 0.02 mW. The temperature range of DSC given in Table 1 matches the uncertainty of ±5°C of the equipment.

Calibration for temperature and enthalpy were made using indium with purity of 99.99%.

2.3. Calorimeter

A Tronac, Model 1250 titration calorimeter was employed, as well as an isoperibol titration calorimeter, Model 458, at 298.15 K with a temperature fluctuation of 0.0003 K. Glass ampules were used to collect the solid reactants. A value of -0.18 ± 0.05 J was determined from the blank experiments. The accuracy and precision of the calorimeter were calibrated by dissolution of tris(hydroxymethyl) aminomethane (G.R.) in 0.1000 mol dm^{-1} HCl (aq). The average enthalpy of reaction was -245.5 ± 0.6 J g^{-1}. This is in good agreement with the value reported by the NBS (-245.8 ± 0.2 J g^{-1}).

3. Results and discussion

3.1. Result of DSC

There were two endothermic and one exothermic peaks in every DSC curve of the four heteropoly acids. Three stages of weight loss were found correspond-

Table 1
Temperature ranges of the thermal effects at DSC curves and the number of water-molecule loss measured from TG curves

Heteropoly acid	Endothermic 1		Endothermic 2			Exothermic	
	t (°C)	$-H_2O$	t (°C)	t_p (°C)	$-H_2O$	t (°C)	$-H_2O$
$H_3PW_{12}O_{40}\cdot 20.0H_2O$	40∼130	14.0	165∼310	280	6.0	560∼600	1.5
$H_4SiW_{12}O_{40}\cdot 6.0H_2O$	40∼125	0.5	160∼310	235	5.5	390∼550	2.0
$H_3PMo_{12}O_{40}\cdot 8.6H_2O$	40∼100	2.8	100∼220 [a]	150, 170	5.8	435∼455	1.5
$H_4SiMo_{12}O_{40}\cdot 12.0H_2O$	40∼100	6.1	100∼220 [a]	125, 165	5.9	365∼385	2.0

[a] Split peak.

ingly at TG curves. The exothermic peak characterizes the collapse of the Keggin unit while the structural water evolves. Table 1 shows the temperature ranges of the three thermal effects in DSC curves. The figures at the right-hand side of a temperature region are the number of water molecules calculated from the weight loss measured by TG.

As discussed previously by infrared analysis, the Keggin anion was still stable at temperatures higher than the offset of the endothermic peaks, except that crystallized water escaped [2,5]. The results shown in Table 1 indicate that the molecules of water in the heteropoly acids can be classified into three parts:

1. In the first weight-loss step, free crystallized water evolved when the temperature was raised, the endothermic peak 1 emerged at DSC curve. It should be noted that the content of water differed from each other. Experimentally, the amount of water of a heteropoly acid is not easy to be controlled exactly in synthesis. It depends on the species and the condition of preparation of an acid. This is the reason why different researchers have reported differing numbers for water of crystallization for the same heteropoly acid.
2. The data calculated from the TG curves indicated that six molecules of water were contained in the second stage, i.e. the 'endothermic 2', no matter which acid it was and how many molecules of water had escaped in the first step. On the other hand, the temperature ranges of HPW were close to those of HSiW, except for the difference between their peak temperatures; the ranges of HPMo and HSiMo were very similar. It should be pointed out that, the second endothermic peaks of molybdenum-containing acids followed the first one immediately, and the second endothermic peaks of HPMo and HSiMo split some what at the top. Obviously, the combination of these six molecules of water with the heteropoly acid is affected mainly by the coordination metal atom, but almost independent of the central heteroatom. The water molecules probably combine with H^+, forming hydroxonium $H(H_2O)_n^+$ [9]. The cations are located outside the framework of heteropoly acid, thus the 12 metal-oxygen octahedrons, which surround the central tetrahedron anion, take more direct and important role in keeping the combined water to the Keggin unit.
3. The third step in DSC curve was an exothermic peak, characterizing the collapse of the Keggin heteropoly anion. Correspondingly, 1.5 (or 2.0) molecules of structural water was lost in the TG curve.

At this stage, the contribution to the temperature in DSC or DTG curves comes from both the coordinated and central atoms. Generally speaking, tungsten-containing heteropoly acids are more stable than molybdenum ones, and phosphoric heteropoly acids are more stable than silicic ones.

The combination of $H(H_2O)_n^+$ with $PW_{12}O_{40}^{3-}$ (or $SiW_{12}O_{40}^{4-}$) is strong enough so that the combined water can be released only at higher temperatures, and exhibits a single but wider endothermic peak at DSC curve. As to the split of the second peaks of HPMo and HSiMo, it should probably be explained with the different types of oxygen-metal combination at the Keggin unit: $O{=}M_+$, $M{-}O{-}M_{edge}$, and $M{-}O{-}M_{corner}$ [2]. Since the connection of $H(H_2O)_n^+$ to $PMo_{12}O_{40}^{3-}$ (or $SiMo_{12}O_{40}^{4-}$) is weaker than to tungsten-containing anions, the interactions between the hydroxonium cation and the different sites on the molybdenum-containing anion can be distinguished at the DSC curve, and a split peak emerges.

In the light of the temperature at which the Keggin anion structure collapses and the temperature of endothermic 2, the order of the thermal stability of these four heteropoly acids should be HPW > HSiW > HPMo > HSiMo.

3.2. Enthalpies of formation

There were only a few reports about the enthalpy of formation of the heteropoly acids published in the literature. Since the anhydrous heteropoly acid has low solubility and low solution rate in water or in dilute alkaline solution, it is experimentally almost impossible to determine the formation enthalpy of an anhydrous heteropoly acid. In this paper, the standard molar enthalpies of formation of four hydrated heteropoly acids were determined calorimetrically in solution. Thermodynamic cycles were designed for determining the formation enthalpies of these four heteropoly acids. If HSiW is taken as an example, then the heats of following reactions are:

$$\begin{aligned}&H_4SiW_{12}O_{40}\cdot 6H_2O(s)\\&\quad +1356[NaOH+73.52H_2O](sol.1)\rightarrow\\&[Na_2SiO_3+12Na_2WO_4+(1356-26)NaOH\\&\quad +(21+1356\times 73.52)H_2O](sol.) \qquad (1)\end{aligned}$$

$$\begin{aligned}&Na_2SiO_3\cdot 9H_2O(s)+12(Na_2WO_4\cdot 2H_2O)(s)\\&\quad +[(1356-26)NaOH\\&\quad +(1356\times 73.52-12)H_2O](sol.2)\rightarrow\\&[Na_2SiO_3+12Na_2WO_4+(1356-26)NaOH\\&\quad +(21+1356\times 73.52)H_2O](sol.) \qquad (2)\end{aligned}$$

$$\begin{aligned}&1356NaOH(s)+1356\times 73.52H_2O(l)\rightarrow\\&\quad 1356[NaOH+73.52H_2O](sol.1) \qquad (3)\end{aligned}$$

$$\begin{aligned}&(1356-26)NaOH(s)\\&\quad +(1356\times 73.52-12)H_2O\rightarrow\\&[(1356-26)NaOH\\&\quad +(1356\times 73.52-12)H_2O](sol.2) \qquad (4)\end{aligned}$$

Eq.(1)–Eq.(2)+Eq.(3)–Eq.(4):

$$\begin{aligned}&H_4SiW_{12}O_{40}\cdot 6H_2O(s)+26NaOH(s)\\&\quad +12H_2O(l)\rightarrow Na_2SiO_3\cdot 9H_2O(s)\\&\quad +12(Na_2WO_4\cdot 2H_2O)(s). \qquad (5)\end{aligned}$$

The original calorimetric measurements of the heats of reaction (1) and (2) are given in Tables 2 and 3, respectively.

On the other hand, the enthalpies of formation and of solution in Eqs. (3) and (4) can be found in literature [10]. The heats of reactions can be obtained as:

$$\Delta H_3 = 1356\times(-44.099)\,\mathrm{kJ\,mol^{-1}};$$
$$\Delta H_4 = 1330\times(-44.091)\,\mathrm{kJ\,mol^{-1}}.$$

Therefore,

$$\begin{aligned}\Delta H_5 &= \Delta H_1-\Delta H_2+\Delta H_3-\Delta H_4\\&= -630.2\,\mathrm{kJ\,mol^{-1}}-217\,\mathrm{kJ\,mol^{-1}}\\&\quad -59.80\times 10^3\,\mathrm{kJ\,mol^{-1}}+58.64\\&\quad \times 10^3\,\mathrm{kJ\,mol^{-1}}\\&= -(2.01\pm 0.02)\times 10^3\,\mathrm{kJ\,mol^{-1}}.\end{aligned}$$

All the standard molar enthalpies of formation $\Delta_f H_m$ of the compounds in Eq. (5), except $H_4SiW_{12}O_{40}\cdot 6H_2O(s)$, are found in [10]. Obviously, the enthalpy of formation of HSiW can be hereby calculated. Similarly, the formation enthalpies of HPMo, HSiMo, and HPW have been determined. The data are as follows,

$$\Delta_f H^o_m(H_3PW_{12}O_{40}\cdot 25.0H_2O) = -(18.58\pm 0.02)\times 10^3\,\mathrm{kJ\,mol^{-1}}$$

$$\Delta_f H^o_m(H_3PW_{12}O_{40}\cdot 20.0H_2O) = -(17.20\pm 0.02)\times 10^3\,\mathrm{kJ\,mol^{-1}}$$

$$\Delta_f H^o_m(H_4SiW_{12}O_{40}\cdot 6.0H_2O) = -(13.14\pm 0.02)\times 10^3\,\mathrm{kJ\,mol^{-1}}$$

$$\Delta_f H^o_m(H_4SiMo_{12}O_{40}\cdot 12.0H_2O) = -(13.92\pm 0.02)\times 10^3\,\mathrm{kJ\,mol^{-1}}$$

$$\Delta_f H^o_m(H_3PMo_{12}O_{40}\cdot 8.6H_2O) = -(12.72\pm 0.02)\times 10^3\,\mathrm{kJ\,mol^{-1}}.$$

It is easy to understand that the data include the contribution of the free crystallized water, and depend upon the amount of water. Provided that the enthalpy of formation of the heteropoly acid can be simply regarded as the sum of the Keggin structure and the water molecules; and if the value of -292 kJ mol^{-1} is

Table 2
The heat of reaction (1) – $H_4SiW_{12}O_{40}\cdot 6H_2O(s)+NaOH$ (0.7556 mol dm^{-3})

Run	W_{HSiW} (mg)	V_{NaOH} (ml)	ΔH^a (J)	ΔH^b (J)	ΔH_1 (kJ mol^{-1})
1	46.47	27.88	−9.91	−9.73	−625.4
2	51.88	31.13	−11.19	−11.01	−633.8
3	49.36	29.62	−10.50	−10.32	−624.4
4	51.85	31.11	−11.24	−11.06	−637.0
Mean					−630.2±6.2

[a] Heat of reaction measured.
[b] Heat of reaction corrected with blank experiments.

Table 3
The heat of reaction (2) – $Na_2SiO_3{\cdot}9H_2O(s)+12Na_2WO_4{\cdot}2H_2O(s)+NaOH$ (0.7412 mol dm^{-3})

Run	W_{NaSiO} (mg)	W_{NaWO} (mg)	V_{NaOH} (ml)	ΔH [a] (J)	H_1 (kJ mol^{-1})
1	5.30	73.82	33.46	4.04	217
2	4.45	61.98	28.07	3.32	212
3	5.25	73.12	33.15	4.03	218
4	4.55	63.37	28.73	3.54	221
Mean					217±3

[a] Heat of reaction corrected with blank experiments.

Table 4
The enthalpy of formation of 6-hydrated and anhydrous heteropoly acids estimated from the experimental data

$\Delta_f H_m$ (10^3 kJ mol^{-1})			
$H_4SiW_{12}O_{40}{\cdot}6H_2O$	−13.14	$H_4SiW_{12}O_{40}$	−11.39
$H_3PW_{12}O_{40}{\cdot}6H_2O$ [a]	−13.03	$H_3PW_{12}O_{40}$ [a]	−11.28
$H_3PW_{12}O_{40}{\cdot}6H_2O$ [b]	−13.11	$H_3PW_{12}O_{40}$ [b]	−11.36
$H_4SiMo_{12}O_{40}{\cdot}6H_2O$	−12.19	$H_4SiMo_{12}O_{40}$	−10.44
$H_3PMo_{12}O_{40}{\cdot}6H_2O$	−11.98	$H_3PMo_{12}O_{40}$	−10.23

[a] Calculated from $H_3PW_{12}O_{40}{\cdot}25H_2O$.
[b] Calculated from $H_3PW_{12}O_{40}{\cdot}20H_2O$.

taken as $\Delta_f H_m$ (H_2O)[solid] [10], it is possible to derive and estimate the formation enthalpy of a heteropoly acid at a comparable and reasonable basis, i.e. six hydrated and anhydrous forms, as shown in Table 4.

It is found from Table 4 that the contribution of the central atom to the enthalpy of formation is less than that of the coordination atom. These two anhydrous tungsten-containing heteropoly acids have very close data of about -11.3×10^3 kJ mol^{-1}. Comparatively, the data of anhydrous molybdenum-containing acids are about -10.3×10^3 kJ mol^{-1}.

On the other hand, the enthalpy of formation of a heteropoly acid can also be estimated in another way. As an example, the enthalpy of formation of anhydrous $H_4SiMo_{12}O_{40}$ is not available in literature by now. When one considers the hydrated molybdosilicic acid as an 'assembly' of components MoO_3, H_4SiO_4 and H_2O according to its structure, then it is very interesting to find that the estimated value of $\Delta_f H_m$ of $H_4SiMo_{12}O_{40}$ in Table 4 is very close to the sum of the enthalpies of formation of its fundamental units. Table 5 shows the data of $\Delta_f H_m$ cited from literature and the results calculated as $\Delta_f H_m$ (heteropoly acid)=12 × $\Delta_f H_m$ (WO_3 or MoO_3) + $\Delta_f H_m$ (H_3PO_4 or H_4SiO_4).

Only a few of heteropoly acids have been reported in respect of their enthalpies of formation so far, but the enthalpy data of their components from which the heteropoly acid is 'assembled' can easily be found in the literature. The correspondence between data of Tables 4 and 5 implies that the enthalpy of formation of similar heteropoly acids, perhaps, can be predicted and estimated in the aforementioned way in the absence of its value.

4. Conclusions

Three steps can be found when the four hydrated heteropoly acids are determined by using DSC and TG methods. In the first two stages, water evolves out of

Table 5
The enthalpy of formation of heteropoly acids calculated from the related compounds

$\Delta_f H_m$ (kJ mol^{-1})			
Reference [10]		Calculated	
WO_3	−842.87	$H_4SiW_{12}O_{40}$	12×(−842.87)−1481.1=−11.595×10^3
MoO_3	−745.09	$H_3PW_{12}O_{40}$	12×(−842.87)−1279.0=−11.393×10^3
H_3PO_4	−1279.0	$H_4SiMo_{12}O_{40}$	12×(−745.09)−1481.1=−10.422×10^3
H_4SiO_4	−1481.1	$H_3PMo_{12}O_{40}$	12×(−745.09)−1279.0=−10.220×10^3

the acids, the second stage corresponds to the loss of six molecules of water. The third stage characterizes the collapse of the Keggin unit, and 1.5 or 2.0 (for phosphoric hetero- or silicic hetero-acid, respectively) molecules of structural water escape at the same time. The general formula of hydrated heteropoly acids can be expressed as $[(1.5H_2O$ or $2H_2O)\cdot(0.5P_2O_5$ or $SiO_2)\cdot 12MO_3\cdot 6H_2O]xH_2O$, where M=W or Mo, x depends on the species and the condition of preparation of an acid.

According to the temperature at which the Keggin anion structure collapses and the temperature of endothermic peak 2, the order of the thermal stability of these four heteropoly acids should be HPW > HSiW > HPMo > HSiMo.

Despite the original content of water in a hydrated heteropoly acid, the $\Delta_f H_m$ of anhydrous $H_3XM_{12}O_{40}$ (X=P or Si; M=W or Mo) have been derived and estimated according to the data obtained by calorimetry. The estimated values are in good accordance with that calculated from the related compounds, WO_3, MoO_3, H_3PO_4 and H_4SiO_4.

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