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Thermal analyses and enthalpies of formation of $H_3PW_{12}O_{40} \cdot 20H_2O$ and $H_3PW_{12}O_{40} \cdot 6DMF \cdot 2H_2O$

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Abstract

TG–DTA techniques were used to determine the compositions and thermal properties of 12-tungstophosphoric acid $H_3PW_{12}O_{40} \cdot 20H_2O$ and its adduct $H_3PW_{12}O_{40} \cdot 6DMF \cdot 2H_2O$. Thermodynamic cycles were designed to measure the standard molar enthalpies of $H_3PW_{12}O_{40} \cdot 20H_2O$ and $H_3PW_{12}O_{40} \cdot 6DMF \cdot 2H_2O$. The heats of reaction were determined by a titration calorimeter. The enthalpies of formation at 298.15 K are $\Delta_f H_m^{\ominus}(H_3PW_{12}O_{40} \cdot 20H_2O) = -(17.20 \pm 0.01) \times 10^3$ kJ mol^{-1}; and $\Delta_f H_m^{\ominus}(H_3PW_{12}O_{40} \cdot 6DMF \cdot 2H_2O) = -(13.64 \pm 0.01) \times 10^3$ kJ mol^{-1}.

INTRODUCTION

Heteropoly acids have significant catalytic activities [1]. Among them, tungstophosphoric acid and its derivatives have been used most extensively. As catalysts, an understanding of their thermal behavior is very important. Qu and Zhou [2] reported that dehydration of 12-tungstophosphoric acid involves three steps, the third ending while the Keggin structure was destroyed. It is reported here, however, that the dehydration process finishes earlier. The value of the enthalpy of formation, a most useful parameter, has not been reported in the literature so far. Using this, a series of $\Delta_f H_m^{\ominus}$ values of its salts and adducts can be determined more easily.

A commonly used compound, dimethylformamide (DMF), was chosen as an example of adduct formation. Thermal and chemical analyses, and the standard molar enthalpy of formation of the adduct have also been studied.

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EXPERIMENTAL

12-Tungstophosphoric acid and its DMF adduct were synthesized according to the methods of Booth [3] and Ding [4]. Tungsten and phosphorus were analysed by gravimetric methods using cinchonine and ammonium magnesium phosphate, respectively. Thermogravimetric and chemical analyses, and the results obtained by igniting the samples at 800°C gave the compositions as $H_3PW_{12}O_{40} \cdot 20H_2O$ and $H_3PW_{12}O_{40} \cdot 6DMF \cdot 2H_2O$.

The elemental analyzer was a Perkin–Elmer 240 and the TG–DTA equipment was a Rigaku Thermoflex, using a dynamic nitrogen atmosphere.

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 ampoules were used to contain the samples. A value of -0.27 ± 0.06 J was determined from the blank experiments. The values reported in this paper are corrected. The accuracy and precision of the calorimeter were tested by dissolution of THAM (tris(hydroxymethyl) aminomethane) (G.R.) in 0.1 mol dm^{-3} HCl (aq). The average enthalpy of reaction was -245.7 ± 0.9 J g^{-1}. This is in good agreement with the value reported by the NBS (-245.8 ± 0.2 J g^{-1}) [5].

RESULTS AND DISCUSSION

Thermal analyses

Figure 1 shows the TG and DTA curves of $H_3PW_{12}O_{40} \cdot 20H_2O$. The weight losses of the three steps were 7.9%, 3.3% and 0.9%, respectively.

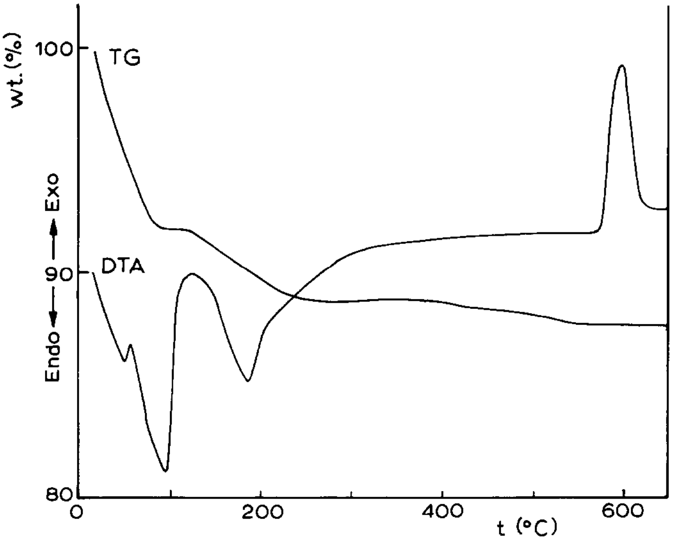

Fig. 1. TG and DTA curves of $H_3PW_{12}O_{40} \cdot 20H_2O$. Dynamic nitrogen atmosphere, 5°C min^{-1}.

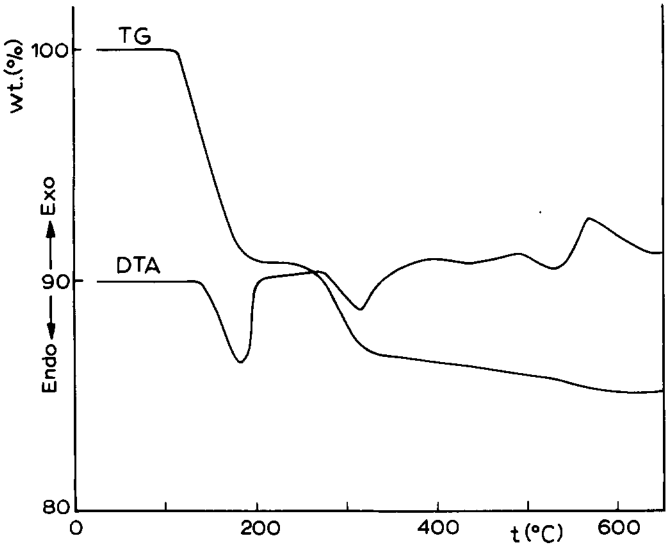

Fig. 2. TG and DTA curves of $H_3PW_{12}O_{40}\cdot 6DMF\cdot 2H_2O$. Dynamic nitrogen atmosphere, 5°C min^{-1}.

The third loss of water took place over such a wide temperature range that its endothermic peak could hardly be found. As reported, the first step corresponds to loss of water, the content of which varies with the circumstances; the second and third losses are of the crystallization and "constitution" water [2,4,6]. Qu and Zhou [2] and Ding [4] reported that the exothermic peak lies at 588°C and 580°C, and that the third water loss ends at 588°C and 600°C, respectively. Thus, the exothermic peak either overlaps with the weight loss process [2] or is covered by it [4]. However, in this paper, it can be clearly observed on the TG and DTG curves that the loss of the constitution water was complete below 580 ± 5°C, about 10°C lower than the extrapolated temperature of the exothermic peak referring to the destruction of the Keggin structure. Indeed, as shown in Fig. 1, the TG curve is almost horizontal after 540°C.

The thermograms of $H_3PW_{12}O_{40}\cdot 6DMF\cdot 2H_2O$ are shown in Fig. 2. The DTA curve shows four endothermic peaks and one exothermic peak. There were two steps on the TG curve corresponding to the first and second peaks, the weight losses being 8.9% and 4.0%. The third step includes several stages which are almost continuous. The total weight loss in this step is 1.7%. A future investigation will attempt to identify the causes of these weight losses.

Enthalpies of formation

To measure the enthalpies of formation of $H_3PW_{12}O_{40}\cdot 20H_2O$ and its adduct $H_3PW_{12}O_{40}\cdot 6DMF\cdot 2H_2O$, the thermodynamic cycles shown in

TABLE 1

Reaction scheme for calculation of $\Delta_f H_m^{\ominus}(H_3PW_{12}O_{40}\cdot 20H_2O)$

$$H_3PW_{12}O_{40}\cdot 20H_2O(s) + n[NaOH + 59.59H_2O](soln.\ 1)\ ^{a,b} \rightarrow$$
$$[Na_3PO_4 + 12Na_2WO_4 + (n-27)NaOH + (35 + 59.59n)H_2O](soln.) \tag{1}$$
$$Na_2HPO_4\cdot 12H_2O(s) + 12Na_2WO_4(s)$$
$$+ (n-26)\{NaOH + [(22 + 59.59n)/(n-26)]H_2O\}(soln.\ 2)\ ^{c} \rightarrow$$
$$[Na_3PO_4 + 12Na_2WO_4 + (n-27)NaOH + (35 + 59.59n)H_2O](soln.) \tag{2}$$
$$NaOH(s) + 59.59H_2O(l) \rightarrow [NaOH + 59.59H_2O](soln.\ 1) \tag{3}$$
$$NaOH(s) + [(22 + 59.59n)/(n-26)]H_2O(l) \rightarrow$$
$$\{NaOH + [(22 + 59.59n)/(n-26)]H_2O\}(soln.\ 2) \tag{4}$$
$$(1) - (2) + n(3) - (n-26)(4):$$
$$H_3PW_{12}O_{40}\cdot 20H_2O(s) + 26NaOH(s) \rightarrow$$
$$Na_2HPO_4\cdot 12H_2O(s) + 12Na_2WO_4(s) + 22H_2O(l) \tag{5}$$

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[a] $n = 1765$.
[b] Soln. 1 = 0.9325 mol dm^{-3}.
[c] Soln. 2 = 0.9280 mol dm^{-3}.

Tables 1 and 2 were designed. In all cases, the reactions were fast enough to fit the titration calorimeter.

According to the data shown in Tables 1, 2, and 3, the heats of reactions (5) and (9) are $\Delta H_5 = -(1902 \pm 9)$ kJ mol^{-1}; and $\Delta H_9 = -(141.6 \pm 6.1)$ kJ mol^{-1}.

TABLE 2

Reaction scheme for calculation of $\Delta_f H_m^{\ominus}(H_3PW_{12}O_{40}\cdot 6DMF\cdot 2H_2O)$

$$H_3PW_{12}O_{40}\cdot 20H_2O(s) + nDMF(l) \rightarrow$$
$$[H_3PW_{12}O_{40} + nDMF + 20H_2O](soln.)\ ^{a} \tag{6}$$
$$H_3PW_{12}O_{40}\cdot 6DMF\cdot 2H_2O(s) + [(n-6)DMF + 18H_2O](soln.) \rightarrow$$
$$[H_3PW_{12}O_{40} + nDMF + 20H_2O](soln.) \tag{7}$$
$$(n-6)DMF(l) + 18H_2O(l) \rightarrow$$
$$[(n-6)DMF + 18H_2O](soln.) \tag{8}$$
$$(6) - (7) - (8):$$
$$H_3PW_{12}O_{40}\cdot 20H_2O(s) + 6DMF(l) \rightarrow$$
$$H_3PW_{12}O_{40}\cdot 6DMF\cdot 2H_2O(s) + 18H_2O(l) \tag{9}$$

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[a] $n = 2.016 \times 10^4$.

TABLE 3

Heats of reaction and formation

Reaction	$-\Delta H^\ominus$ (kJ)	Compound	$-\Delta_f H_m^\ominus$ (kJ mol^{-1})	Ref.
(1)	801.1 ± 6.9	$H_2O(l)$	285.83	7
(2)	47.4 ± 2.5	Na_2WO_4	1548.9	7
(3) and (4) [a]	44.17	$Na_2HPO_4 \cdot 12H_2O(s)$	5297.8	7
(5)	1902 ± 9	NaOH(s)	425.61	7
(6)	227.5 ± 4.3	DMF(l)	239.37	8
(7)	23.6 ± 1.5	$H_3PW_{12}O_{40} \cdot 20H_2O(s)$	17.20×10^3	
(8)	62.3 ± 6.2	$H_3PW_{12}O_{40} \cdot 6DMF \cdot 2H_2O(s)$	13.64×10^3	
(9)	141.6 ± 6.1			

[a] Calculated from ref. 7.

The standard molar enthalpies of formation are $\Delta_f H_m^\ominus = -(17.20 \pm 0.01) \times 10^3$ kJ mol^{-1} for $H_3PW_{12}O_{40} \cdot 20H_2O$; and $\Delta_f H_m^\ominus = -(13.64 \pm 0.01) \times 10^3$ kJ mol^{-1} for $H_3PW_{12}O_{40} \cdot 6DMF \cdot 2H_2O$. The uncertainties are the standard errors of the mean.

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