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THE ENTHALPIES OF FORMATION AND EVOLVED GAS DETECTION
$H_4SiW_{12}O_{40}\cdot 6H_2O$ and its DMF and DMSO adducts

Meiling Huang [2], *Xian'e Cai* [1*], *Daichun Du* [1], *Youming Jin* [1], *Jing Zhu* [1], *Zemin Lin* [3]

[1]Department of Chemistry, Fudan University, Shanghai 200433
[2]Shanghai Institute of Chemical Technology, Shanghai 200233
[3]Scientific Research Institute of Fragrance & Flavor, Shanghai 200031, P. R. China

Abstract

The standard molar enthalpies of formation of $H_4SiW_{12}O_{40}\cdot 6H_2O$ (I), $H_4SiW_{12}O_{40}\cdot 6DMF\cdot H_2O$ (II), $H_4SiW_{12}O_{40}\cdot 8DMSO\cdot H_2O$ (III) have been determined. Thermodynamic cycles were designed, and the heat of reactions in the thermodynamic cycles were measured calorimetrically. The infrared spectra were compared with those of the heteropoly anion α-$H_4SiW_{12}O_{40}$ [1] and of the ligands DMF and DMSO. The evolved gas from the adducts was monitored by a quadrupole mass spectrometer at a heating rate of 16 deg·min^{-1}.

Keywords: dimethylformamide (DMF), dimethylsulfoxide (DMSO), enthalpy of formation, evolved gas detection, IR, tungstosilicic acid

Introduction

As a helpful redox catalyst, tungsten-containing poly acids are employed in reactions in the homogeneous liquid phase and in the heterogeneous gas-solid phase [2]. Their thermal properties, however, are still very little known. A number of the isopoly and heteropoly acids and their adducts have been reported [3–6]. In this paper, $H_4SiW_{12}O_{40}\cdot 6H_2O$ (I), $H_4SiW_{12}O_{40}\cdot 6DMF\cdot H_2O$ (II), $H_4SiW_{12}O_{40}\cdot 8DMSO\cdot H_2O$ (III) were synthesized and analysed. In addition to their enthalpies of formation, their infrared spectra were given as well. The evolved gases from the samples in vacuo were monitored with a temperature-programmed quadrupole mass spectrometer. Their enthalpies of formation and thermal behaviour reported here will be helpful for estimating other chemical and thermodynamic data, and hence the application of the tungsten-containing compounds will be promoted.

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* To whom correspondence should be addressed.

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Experimental

Apparatus

A Tronac Model-1250 titration calorimeter, with its Model-458 isoperibol accessory, was employed to determine the heats of the reactions at 298.15±0.0003 K. The operation conditions and the calibration of the calorimeter were the same as in a previous work [4].

Du Pont-1090 and CDR-1 (a product of the Shanghai Balance Equipment Factory, Shanghai, China) were used for TG and DSC determination, respectively.

Infrared spectra were recorded as KBr pellets on a Nicolet 5DX FTIR.

Finnigan Mat-4515 quadrupole gas chromatograph/mass spectrometer with a temperature-programmed accessory was used to monitor the evolved gas when the sample was heated at the rate of 16 deg·min^{-1} in vacuo.

Syntheses and analyses

Most of the reagents were purchased form the No.1 Reagent Factory of Shanghai, China, in A.R. grade, and used without any further purification. DMF and DMSO were dried with 5A molecular sieves.

The heteropoly acid (**I**) was obtained by a reaction of Na_2WO_4 and Na_2SiO_3 in concentrated HCl media according to the methods of Booth [5] and Ding [6]. To a mixture of acetonitrile (3.0 ml) and water (1.0 ml), 20 g of (**I**) and double stoichiometric amounts of DMF or DMSO were added at 70°C. 10 min later, the solution was cooled to room temperature, and kept in a big box at 10–15°C for 30 days. Crystals of (**II**) and (**III**) were obtained. The bonds between the added ligands and the Keggin structure of the heteropoly acid were identified by IR.

The contents of silica and tungsten oxide were analysed by gravimetric methods. Carbon, nitrogen and hydrogen were determined, using a Perkin-Elmer Elemental Analyzer PE-240. The hydration number of the crystal water and the additive ligand were also confirmed by TG and DSC.

The cell parameter of (**III**) was determined using an Enraf-Nonius CAD-4 X-ray diffractometer: $a=b=1.7467$ nm, $c=1.8528$ nm, $\alpha=\beta=90°$, $\gamma=120°$.

Results and discussion

Enthalpies of formation

A thermodynamic cycle consisting of 5 reactions, which was similar to the case of tungstophosphoric acid [4], was used to measure $\Delta_f H_m$ (**I**). Another two schemes consisting of 4 reactions each were designed to determine $\Delta_f H_m$ (**II**) and $\Delta_f H_m$ **(III)**. These latter two schemes can also be compared with that in determining the enthalpy of formation of $H_3PW_{12}O_{40}\cdot 6DMF\cdot H_2O$ [4]. In all cases, the reactions were fast enough for the titration calorimeter. From the cycles, the heats of the following reactions were hereby calculated:

$$\begin{aligned}&\textbf{(I)}\ (s)+26NaOH\ (s)+12H_2O\ (l)\rightarrow\\&Na_2SiO_3\cdot 9H_2O\ (s)+12Na_2WO_4\cdot 2H_2O\ (s)\end{aligned}\qquad(1)$$

$$\textbf{(I)}\ (s)+6DMF\ (l)\rightarrow\textbf{(II)}\ (s)+5H_2O\ (l)\qquad(2)$$

$$\textbf{(I)}\ (s)+8DMSO\ (l)\rightarrow\textbf{(III)}\ (s)+5H_2O\ (l)\qquad(3)$$

$$\Delta_r H_m\,(1) = -(2004\pm 7)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_r H_m\,(2) = -(190.3\pm 6.9)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_r H_m\,(3) = -(248.6\pm 7.2)\ \mathrm{kJ\cdot mol^{-1}}$$

All the standard molar enthalpies of formation $\Delta_f H_m$ of the compounds mentioned above, except **(I)**, **(II)** and **(III)**, are found in literatures [10, 11]. Obviously, the enthalpies of formation **(I)**, **(II)** and **(III)** can be hereby calculated. Their values are:

$$\Delta_f H_m(H_4SiW_{12}O_{40}\cdot 6H_2O) = -(13.14\pm 0.01)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_f H_m(H_4SiW_{12}O_{40}\cdot 6DMF\cdot H_2O) = -(13.61\pm 0.01)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_f H_m(H_4SiW_{12}O_{40}\cdot 8DMSO\cdot H_2O) = -(13.86\pm 0.01)\ \mathrm{kJ\cdot mol^{-1}}$$

Infrared spectra

The data shown in the first and second columns of Table 1 are in good agreement. These absorption bands are expected to appear in the spectra of **(II)** and **(III)**, for the coordination bond is so weak that the heteropoly acid anion keeps its Keggin structure almost intact. However, the shifts of $\nu(W\text{–}O_d)$ (982 cm^{-1}) and $\nu(W\text{–}O_c)$ (792 cm^{-1}) of **(II)** and **(III)** reveal the fact that coordination weakens the bond $W\text{-}O_d$, but strengthens the bond $W\text{–}O_c$. O_d is the terminal atom of the tungstate octahedron, while O_c connects two octahedrons, 12 of which link each other around the silicate anion. On the other hand, $\nu(C=O)$ of DMF and $\nu(S=O)$ of DMSO have obviously shifted with reduced intensities. These results in Table 1 provide much essential information: first, the ligand does not affect the Keggin structure of the heteropoly acid anion; second, the added ligands coordinate with tungsten or hydrogen mainly via oxygen in this carbonyl or sulfoxide group, and it is also possible that hydrogen bonds exist between atom O_d of the anion and the methyl group of DMF; third, DMSO results in a greater shift than DMF at $\nu(W{-}O_d)$ and $\nu(W{-}O_c)$ it leads to a higher thermal stability.

Table 1 The main infrared absorption bands (cm^{-1}) and their assignments of **(I)**, **(II)** and **(III)**

HSiW*	(I)	DMF	(II)	DMSO	(III)	Assignment [1,9]
		1678vs	1651m			$\nu(CO)+\nu(CN)$
		1500m	1486m			$\delta(CH_3)+\nu(CN)$
		1435m	1439w	1438m	1435m	$\delta(CH)$
		1410m	1416w	1416m	1412m	$\delta(CH)$
		1386s	1384m			$\delta(CH_3)+\nu(CN)$
				1322m	1324m	$\delta(CH)$
		1255s	1251w			$\nu(CN)$
		1090vs	1101w			$\gamma(CH_3)$
				1055s	1030m	$\nu(SO)$
1020m	1021m		1018m		1020m	$\nu(OH)$
982s	982s		976s		972s	$\nu(W\text{-}O_d)$
				952m	953w	$\gamma(CH_3)$
930vs	927vs		925vs		925vs	$\nu(SiO)$
885m	883m		884m		883m	$\nu(W\text{-}O_b)$
792vs	793vs		799vs		801vs	$\nu(W\text{-}O_c)$
		670w	667w			$\delta(OCN)+\nu(CN)$
			592w			$\delta(SiO)$
535m	540m		536m		534m	$\delta(SiO)$
480w	477w		481w		481w	$\delta(SiO)$

*HSiW = α-$H_4SiW_{12}O_{40}$ [1]

Evolved gas detection

Evolved gas was monitored with a quadrupole mass spectrometer when the sample was heated at a rate of 16 deg·min^{-1} from room temperature to 350°C. The operation conditions were as follows, entry sample: solid; scanning range: $m/z=15$ –650; scan time: 3 s; operating pressure: 3.7×10^{-7} torr; ionizer mode; electron voltage: 70 eV; emission current: 0.25 mA; ionization temperature:

140°C; electron multiplier voltage: 1.2 kV. Comparison is undertaken in the following with the results of TG and DSC, in which dynamic nitrogen atmosphere and the heating rate of 10 deg·min^{-1} were used.

$H_4SiW_{12}O_{40}\cdot 6H_2O$ (I)

From the TG curve of (I), a total weight loss of 3.69% was found at the temperature range of 80 to 250°C, with two peaks shown in the DSC curve. The weight loss corresponds to 6 molecules of H_2O. The remaining two molecules of H_2O, the so-called 'constitution' water of the anion, were lost from 390 to 550°C, with an exothermic peak at 530°C denoting the complete destruction of the Keggin structure.

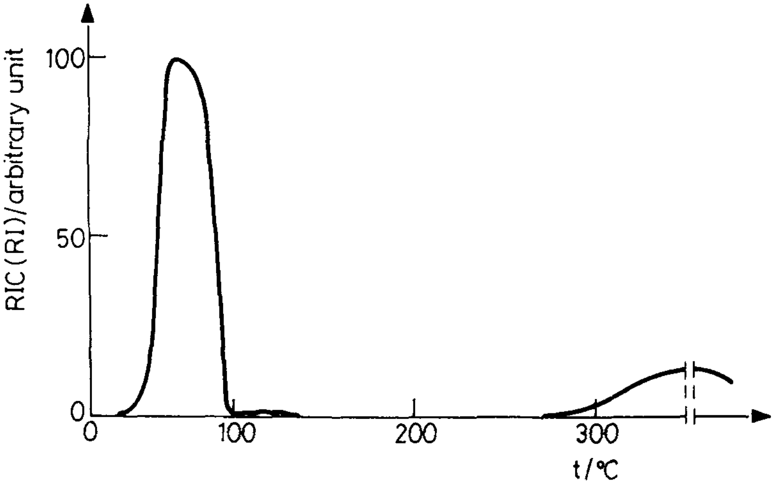

Fig. 1 The temperature-programmed evolved gas detection of sample (I)

The curve of the evolved gas of (I), subtracted from the background, is shown in Fig. 1. According to the mass spectra, water was the only product. Therefore, the relative intensity of the ion current (RIC) was equivalent to the relative intensity (RI) of $m/z=18$, when monitored. Water was evolved almost from beginning of heating, reaching a maximum at 64°C. The first peak without splitting should correspond to $6H_2O$. The evolved temperature range was much lower in vacuo than under normal pressure as done in TG and DSC methods. After 95°C, only a very low RIC was detected. The 'constitution' water started to evolve at about 270°C, also much lower than in the dynamic nitrogen atmosphere. RIC increased with the increase in temperature. 350°C is the upper limit of our equipment. Therefore, RIC decreased afterward, with only 1.3 H_2O evolved in this step.

$H_4SiW_{12}O_{40}\cdot 6DMF\cdot H_2O$ (II)

TG and DSC curves of **(II)** gave results: one molecule of water and one DMF lost from 50 to 110°C, followed by 2 molecules of DMF lost from 110 to 160°C, and then the remaining DMF lost from 400 to 530°C, overlapping with the loss of 2 molecules of 'constitution' water.

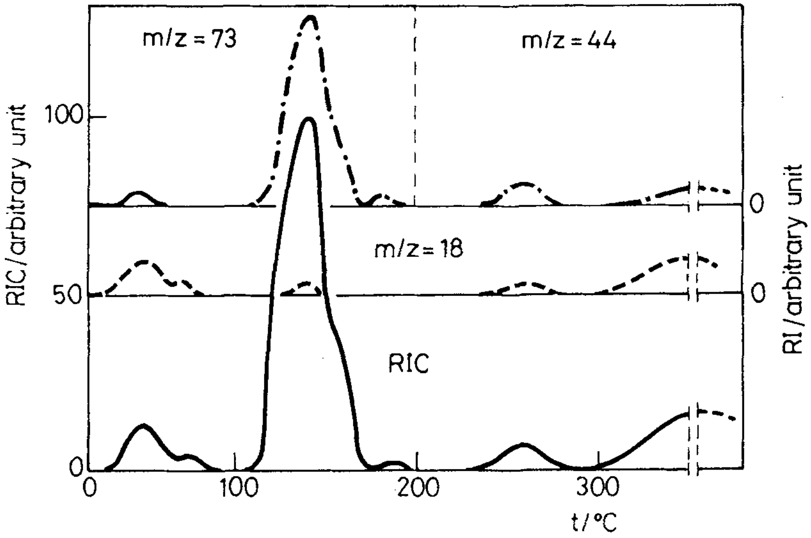

Fig. 2 The temperature-programmed evolved gas detection of sample **(II)**

The curve of the evolved gas of **(II)** as shown in Fig. 2 is more complicated. The lowest curve represents RIC; the middle curve monitored at $m/z=18$; the upper curve monitored at $m/z=73$ (at <200°C), and $m/z=44$ (at>200°C). From the mass spectra, fragments of DMF were found when the temperature was lower than 200°C. As the sample was heated up to higher temperature, the library search of the spectra showed no DMF but dimethyl amine, the main peak was $m/z=44$ with a bit of higher intensities of $m/z=18$ and 28. This could probably be interpreted as: when the temperature is as high as 200°C, DMF which was still coordinated to the heteropoly anion breaks its bonds between $(CH_3)N-$ and $-(C=O)$ first, and then the bonds linking the carbonyl to the acid anion. Therefore, the mass spectrum of DMF disappears completely. In sum, the upper curve shows 5 peaks altogether. At about 50°C, a bit of DMF was detected along with the crystallization water. The principal evolution takes place at 110 to 170°C with a small 'tail'. At the range of 240 to 280°C, and above 300°C, the peaks should be related to the DMF molecules firmly linked to the anion. Because of the difference in decomposition, it is difficult to estimate the accurate amount of DMF molecules which evolved or decomposed from the anion among these steps. However, it should be very interesting to make further investigation on the different bonding energies and active sites on the anion surface in future.

On the other hand, H_2O lost at <95°C and the 'constitution' water loss started at 300°C, both were also lower than the case in TG and DSC. The two small peaks at about 140 and 260°C, perhaps, could be related to partial decomposition of DMF as explained above.

$H_4SiW_{12}O_{40}\cdot 8DMSO\cdot H_2O$ (III)

The TG and DSC curves of **(III)** showed that, one molecule of water was lost at 40 to 90°C. At a narrow temperature range of 180 to 220°C, 6 molecules of DMSO evolved, with three continuous peaks appearing in the DSC curve. The last two DMSO evolved at 420 to 510°C, followed by the destruction of the Keggin structure.

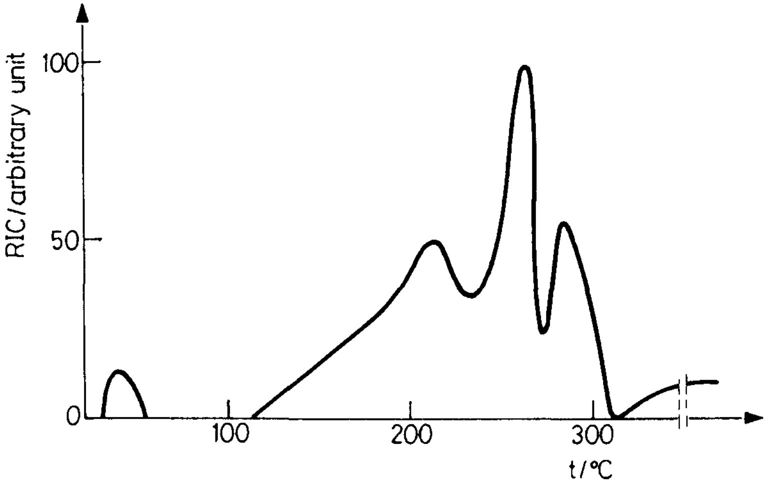

Fig. 3 The temperature-programmed evolved gas detection of sample **(III)**

Figure 3 shows only the RIC of the evolved gas of **(III)**. The first peak appears at 30 to 50°C was due to water. From 110 to 310°C, there are three consecutive peaks, and finally the last begins. In the last peak, not only 'constitution' water but also fragments from DMSO were detected. The difficult situation was that the products of the evolved gas changed according to temperature. The main peaks in a series of spectra which were detected at different temperature shifted from [78, 63... (DMSO)], to [78, 63... plus 79, 94... (dimethyl sulfide)], to [60... (C_2H_4S) plus 18 (H_2O)], and to [76... (C_2H_4OS) plus 18] at last. Some are the decomposition or disproportion products of DMSO. It is also possible to assume that some of the fragments drop away from the adduct before DMSO evolves. The components of the mixture detected change gradually from 110 to 350°C. The curve shows that, as an added ligand, DMSO evolves from the adduct in several steps. It is necessary to point out that the main components of the peaks were: 214°C – DMSO; 262°C – dimethyl sulfone; 282°C – $(CH_2)_2S+H_2O$; >300°C – $H_2O+(CH_2)_2SO$, respectively.

Conclusions

The standard molar enthalpies of tungstosilicic acid and its DMF and DMSO adducts have been determined. The formulae and the enthalpies are:

$$\Delta_f H_m(H_4SiW_{12}O_{40}\cdot 6H_2O) = -(13.14\pm 0.01)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_f H_m(H_4SiW_{12}O_{40}\cdot 6DMF\cdot H_2O) = -(13.61\pm 0.01)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_f H_m(H_4SiW_{12}O_{40}\cdot 8DMSO\cdot H_2O) = -(13.86\pm 0.01)\ \mathrm{kJ\cdot mol^{-1}}$$

The infrared spectra give some information: the Keggin structure of the heteropoly acid anion remains essentially unchanged in the adduct, the main bonding exists between the oxygen of carbonyl or sulfoxide group in DMF or DMSO and tungsten or hydrogen in the heteropoly acid anion.

The detection of evolved gas show that, the crystallization and 'constitution' water, and the added ligands as well, all evolved at much lower temperature in vacuo than under normal pressure. DMSO has stronger bonding than DMF to the heteropoly acid anion, supported by IR. DMSO adduct has a higher thermal stability than DMF adduct. The principal evolution of DMF and DMSO took place at 110 to 170 and at 110 to 310°C, respectively. It would be very useful to make further investigation on the different bonding energies and active sites on the heteropoly acid anion surface in future.

* * *

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Zusammenfassung — Die molaren Standardenthalpien der Bildung von $H_4SiW_{12}O_{40}\cdot 6H_2O$ (I), $H_4SiW_{12}O_{40}\cdot 6DMF\cdot H_2O$ (II) und $H_4SiW_{12}O_{40}\cdot 8DMSO\cdot H_2O$ (III) wurden ermittelt. Es wurden thermodynamische Kreisläufe konstruiert und die Reaktionswärme der thermodynamischen Kreisläufe kalorimetrisch gemessen. Die IR-Spektren wurden mit dem des heteropolaren Anions $H_4SiW_{12}O_{40}$ [1] und mit denen der Liganden DMF und DMSO verglichen. Das aus den Addukten freigesetzte Gas wurde über ein Quadrupol-Massenspektrometer bei einer Aufheizgeschwindigkeit von 16 grad/min verfolgt.