THE ENTHALPIES OF FORMATION AND EVOLVED GAS DETECTION
H₄SiW₁₂O₄₀·6H₂O and its DMF and DMSO adducts

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Abstract

The standard molar enthalpies of formation of H₄SiW₁₂O₄₀·6H₂O (I), H₄SiW₁₂O₄₀·6DMF-H₂O (II), H₄SiW₁₂O₄₀·8DMSO·H₂O (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-H₄SiW₁₂O₄₀ [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, H₄SiW₁₂O₄₀·6H₂O (I), H₄SiW₁₂O₄₀·6DMF·H₂O (II), H₄SiW₁₂O₄₀·8DMSO·H₂O (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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Experimental

Apparatus

A Tronac Model-1250 titration calorimeter, with its Model-458 isoperibol accessory, was employed to determine the heats of the reactions at $298.15 \pm 0.0003$ 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 from 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$_2$WO$_4$ and Na$_2$SiO$_3$ 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, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$.

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 $\Delta_H^m$ (I). Another two schemes consisting of 4 reactions each were designed to determine $\Delta_H^m$ (II)