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A thermochemical study of the reactions of 8-hydroxyquinoline with $Co(Ac)_2{\cdot}4H_2O$ and $Zn(Ac)_2{\cdot}2H_2O$

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Abstract

The solid-state coordination reactions:

$$2HQ(s) + Co(Ac)_2 \cdot 4H_2O(s) \rightarrow Co(HQ)_2 \cdot 2H_2O(s) + 2HAc(l) + 2H_2O(l)$$

$$2HQ(s) + Zn(Ac)_2 \cdot 2H_2O(s) \rightarrow Zn(HQ)_2 \cdot H_2O(s) + 2HAc(l) + H_2O(l)$$

have been studied by solution calorimetry. The molar dissolution enthalpies of the reactants and the products in a certain solvent, 4 mol l^{-1} HCl, of this solid–solid coordination reaction have been measured using an isoperibol calorimeter. From the results and other auxiliary quantities, the standard molar formation enthalpies of [$Co(HQ)_2{\cdot}2H_2O$(s), 298.15 K], [$Zn(HQ)_2{\cdot}H_2O$(s), 298.15 K] and have been determined to be $\Delta_f H_m^{\ominus}$ ($Co(HQ)_2{\cdot}2H_2O$(s), 298.15 K) $= -766.9 \pm 3.0$ kJ mol^{-1}, $Q)_2{\cdot}H_2O$(s), 298.15 K) $= -580.7 \pm 3.0$ kJ mol^{-1}. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: 8-Hydroxyquinoline; Cobalt(II); Zinc(II); Solution calorimetry; Standard molar formation enthalpy

1. Introduction

The compound 8-hydroxyquinoline (HQ) is a very good ligand, forms complex compounds with various metal ions in solution. The strong chelating action of HQ in solution has been extensively studied and widely used in analytical chemistry. The ability of HQ to render metallic ions inactive in trace amounts by chelation seems to be the reason why it acts as bactericides and fungicides [1]. Its copper(II), cobalt(II) and zinc(II) complexes have also been used in industrial applications because of their ability to protect wood and textiles from rot-producing fungi [2]. Thus, the formation of coordination complexes in solution has been well understood, and that has now been extended into solid-state coordination chemistry [3–6]. The products of solid-state reactions between HQ and $Co(Ac)_2{\cdot}4H_2O$, and $Zn(Ac)_2{\cdot}2H_2O$ have been characterized by IR, thermal decomposition and element analyses, and the isothermal kinetics of these reactions were investigated by XRD [4,6]. However, very little is known of the thermochemical properties of the solid-state reaction at ambient temperatures. The object of the present study is to determine the dissolution enthalpies of the reactants and the products of the solid-state coordination reactions by solution calorimetry. The standard molar formation enthalpy of [$Zn(HQ)_2{\cdot}H_2O$(s), 298.15 K] and [$Co(HQ)_2{\cdot}2H_2O$(s),

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298.15 K] have been derived from the respective dissolution enthalpy.

2. Experimental

2.1. Reagents

The compound 8-hydroxyquinoline is abbreviated as HQ. All the chemicals ($Zn(Ac)_2{\cdot}2H_2O$, $Co(Ac)_2{\cdot}4H_2O$, HQ and hydrochloric acid) used were of analytical grade.

KCl, calorimetric primary standard of purity greater than 99.99%, was dried in a vacuum oven for 6 h at 408 K prior to use. Distilled water was used throughout the experiment, it was distilled twice and deionized, the conductivity of the water, κ, is about 1×10^{-4} S m^{-1}.

2.2. Calorimeter

The isoperibol reaction calorimeter used for this study was constructed in this laboratory and was adapted for measuring enthalpies of solid–liquid, liquid–liquid reaction [7,8]; the volume of the reaction vessel is 100 cm^3. The precision temperature control and measurement are ± 0.001 and ± 0.0001 K, respectively.

The calorimeter was tested by measuring the dissolution enthalpy of THAM (NBS 742a, USA) in 0.1 mol l^{-1} HCl and KCl (calorimetric primary standard) in water at 298.15 K. The mean dissolution enthalpies are $-297,766 \pm 16$ J mol^{-1} for THAM and $17,597 \pm 17$ J mol^{-1} for KCl, which are in conformity with the respective published data [9,10].

2.3. Preparations

The compounds $Zn(HQ)_2{\cdot}H_2O(s)$ and $Co(HQ)_2{\cdot}2H_2O(s)$ were prepared and analyzed according to the method given in [6].

3. Results and discussion

3.1. The calorimetric solvent

In this experiment, the 4 mol l^{-1} HCl solution was selected as calorimetric solvent for the reactions of HQ with $Zn(Ac)_2{\cdot}2H_2O$ and $Co(Ac)_2{\cdot}4H_2O$.

3.2. The standard molar formation enthalpy of $Co(HQ)_2{\cdot}2H_2O(s)$

Samples of mass 0.40 g of $CoAc_2{\cdot}4H_2O(s)$ and HQ(s) mixture at mole ratio of $n(CoAc_2{\cdot}4H_2O)$: $n(HQ) = 1{:}2$ were dissolved in 100 ml 4 mol l^{-1} HCl at 298.15 K.

s = calorimetric solvent

$$\{CoAc_2 \cdot 4H_2O(s) + 2HQ(s)\} + \text{`s'} \rightarrow \text{solution A} \quad (1)$$

The dissolution enthalpies of HAc(aq) $\{n(HAc){:}\ n(H_2O) = 1{:}1\}$ in 100 ml 4 mol l^{-1} HCl were measured under the same condition

$$1{:}1\ HAc(aq) + \text{`s'} \rightarrow \text{solution B} \quad (2)$$

The dissolution enthalpies of $Co(HQ)_2{\cdot}2H_2O(s)$ in solution B was measured.

$$Co(HQ)_2 \cdot 2H_2O(s) + \text{`B'} \rightarrow \text{solution A1} \quad (3)$$

The dissolution enthalpies for the reactants and the products are listed in Table 1.

The dissolution enthalpy of the products 2 H_2O in solution A1 lies below the sensitivity of the calorimeter not to measure accurately. Thus, it is ignored and does not affect the experimental result.

The reaction scheme used to derive the standard molar formation enthalpy of $Co(HQ)_2{\cdot}2H_2O(s)$ is given in Table 1. The molar dissolution enthalpies of $CoAc_2{\cdot}4H_2O(s)$ and HQ(s) mixture at mole ratio of $n(CoAc_2{\cdot}4H_2O)$: $n(HQ) = 1{:}2$ was determined in 4 mol l^{-1} HCl. In the same conditions, we have measured the molar dissolution enthalpy of HAc(aq) $\{n(HAc){:}\ n(H_2O) = 1{:}1\}$. Moreover, the molar dissolution enthalpy of $Co(HQ)_2{\cdot}2H_2O(s)$ was determined in B (see in Table 1). These values were combined with auxiliary values of $\Delta_f H_m^\Theta = -2167.54$ kJ mol^{-1} for $CoAc_2{\cdot}4H_2O(s)$ [11], -285.83 ± 0.04 kJ mol^{-1} for $H_2O(l)$ [12], -484.5 kJ mol^{-1} for HAc(l) [13] and -83.0 ± 1.5 kJ mol^{-1} for HQ(s) [14] to derive the standard molar formation enthalpy of $[Co(HQ)_2{\cdot}2H_2O(s)]$: $\Delta_f H_m^\Theta$ ($Co(HQ)_2{\cdot}2H_2O(s)$, 298.15 K) $= -766.9 \pm 3.0$ kJ mol^{-1}.

3.3. The standard molar formation enthalpies of $Zn(HQ)_2{\cdot}H_2O(s)$

According to the method in Section 3.2, the standard molar formation enthalpies of $Zn(HQ)_2{\cdot}H_2O(s)$

Table 1
Reaction scheme for the standard molar formation enthalpy of $Co(HQ)_2 \cdot 2H_2O(s)$ at the temperature 298.15 K[a]

Reaction	Solution	$\Delta_s H_m^\Theta$ (kJ mol^{-1})
1. $\{CoAc_2 \cdot 4H_2O(s) + 2HQ(s)\}$ + ‘s’	A	-28.03 ± 0.04[b]
2. 1 : 1 HAc(aq) + ‘s’	B	-1.505 ± 0.023[b]
3. $Co(HQ)_2 \cdot 2H_2O(s)$ + ‘B’	A1	-47.35 ± 0.01[b]
4. $Hac(l) + H_2O(l) = 1 : 1\,HAc(aq)$		-3.68[c]
5. $2H_2(g) + O_2(g) + 2C(s) = HAc(l)$		-484.5
6. $Co(s) + 4C(g) + 4O_2(g) + 7H_2(g) = CoAc_2 \cdot 4H_2O(s)$		-2167.54
7. $9C(s) + \frac{1}{2}N_2(g) + \frac{7}{2}H_2(g) + \frac{1}{2}O_2(g) = HQ(s)$		-83.0 ± 1.5
8. $H_2(g) + \frac{1}{2}O_2(g) = H_2O(l)$		-285.83 ± 0.04
9. $Co(s) + N_2(g) + 2O_2(g) + 9H_2(g) + 18C(s) = Co(HQ)_2 \cdot 2H_2O(s)$		-766.9 ± 3.0[d]

[a] The solvent ‘s’ was 4 mol l^{-1} HCl. $\Delta H_9 = \Delta H_1 - 2\Delta H_2 - \Delta H_3 - \Delta H_4 - 2\Delta H_5 - 2\Delta H_8 + \Delta H_6 + 2\Delta H_7$.

[b] The mean value of five-times experiments.

[c] According to [15]. $\sigma_a = \sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2/n(n-1)}$, in which n is experimental number ($n = 5$); x_i, experimental value of each series of repeated measurement; $\bar{x}$, mean value.

[d] $\sigma_9 = \sqrt{\sigma_1^2 + 2^2\sigma_2^2 + \sigma_3^2 + 2^2\sigma_8^2 + 2^2\sigma_7^2}$.

has been determined from the reaction scheme as listed in Table 2, respectively. The values $\Delta_f H_m^\Theta$ $(Zn(HQ)_2 \cdot H_2O(s)$, $298.15\ K) = -580.7 \pm 3.0$ kJ mol^{-1} are presented in Table 2.

In this paper, we confirm thermodynamic identity solutions A and A1, C and C1 (see in Tables 1 and 2) by UV spectroscopy and the data of the refrangibility, and used the unique thermochemical cycle with every calorimetric solvent for the reactants and the products of the solid-state coordination reactions. Thus, we believe that $\Delta_f H_m^\Theta$ values determined by solution calorimeter measurements are reliable.

It is difficult to determine the enthalpy change of solid-state reactions, very little is known of the thermochemical properties of the solid-state reaction at ambient temperatures. From the above, we can see that thermochemical properties of the solid-state reaction can be investigated by this iosoperibol calorimetry, it

Table 2
Reaction scheme for the standard molar formation enthalpy of $Zn(HQ)_2 \cdot H_2O(s)$ at the temperature 298.15 K[a]

Reaction	Solution	$\Delta_s H_m^\Theta$ (kJ mol^{-1})
1. $\{Zn(Ac)_2 \cdot 2H_2O(s) + 2HQ(s)\}$ + ‘s’	C	-23.328 ± 0.032[b]
2. 2 : 1 HAc(aq) + ‘s’	D	-2.418 ± 0.025[b]
3. $Zn(HQ)_2 \cdot H_2O(s)$ + ‘D’	C1	-16.329 ± 0.038[b]
4. $2HAc(l) + H_2O(l) = 2 : 1\,Hac(aq)$		-3.59[c]
5. $2H_2(g) + O_2(g) + 2C(s) = HAc(l)$		-484.5[d]
6. $9C(s) + \frac{1}{2}N_2(g) + \frac{7}{2}H_2(g) + \frac{1}{2}O_2(g) = HQ(s)$		-83.0 ± 1.5[e]
7. $Zn(s) + 4C(g) + 3O_2(g) + 5H_2(g) = Zn(Ac)_2 \cdot 2H_2O(s)$		-1668.579[f]
8. $H_2(g) + \frac{1}{2}O_2(g) = H_2O(l)$		-285.83 ± 0.04[f]
9. $Zn(s) + N_2(g) + O_2(g) + 8H_2(g) + 18C(s) = Zn(HQ)_2 \cdot H_2O(s)$		-580.7 ± 3.0[g]

[a] The solvent ‘s’ was 4 mol l^{-1} HCl. $\Delta H_9 = \Delta H_1 - \Delta H_2 - \Delta H_3 - \Delta H_4 - 2\Delta H_5 - \Delta H_8 + 2\Delta H_6 + \Delta H_7$.

[b] The mean value of five-times experiments.

[c] According to [15].

[d] According to [14].

[e] According to [13].

[f] According to [12].

[g] $\sigma_9 = \sqrt{\sigma_1^2 + \sigma_2^2 + \sigma_3^2 + \sigma_8^2 + 2^2\sigma_6^2}$.

is an easy and efficient method for the study of solid-state reactions.

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