

A thermochemical study of the reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with 8-hydroxyquinoline

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Received 18 October 1999; received in revised form 12 March 2000; accepted 14 March 2000

Abstract

The solid-state coordination reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with 8-hydroxyquinoline (HQ): $\text{HQ}(\text{s}) + \text{CuCl}_2 \cdot 2\text{H}_2\text{O}(\text{s}) \rightarrow \text{Cu}(\text{HQ})\text{Cl}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l})$ has been studied by solution calorimetry. The molar dissolution enthalpies of the reactants and the products in 3 mol l^{-1} HCl of the solid–solid coordination reaction have been measured using an isoperibol calorimeter. From the results and other auxiliary quantities, the standard molar formation enthalpy of $[\text{Cu}(\text{HQ})\text{Cl}_2, \text{s}, 298.15 \text{ K}]$ at 298.15 K has been derived: $\Delta_f H_m^\ominus(\text{Cu}(\text{HQ})\text{Cl}_2, \text{s}, 298.15 \text{ K}) = -340.12 \text{ kJ mol}^{-1}$. © 2000 Elsevier Science B.V. All rights reserved.

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

1. Introduction

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. In recent decades, the formation of coordination complexes in solution has been well understood, and this has now been extended into solid-state coordination chemistry [1–6]. Its copper (II) complexes have also been used in industrial applications because of their ability to protect wood and textiles from rot-producing fungi [7]. The solid-state reaction between 8-hydroxyquinoline and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ has been studied. The reaction product

has been characterised by IR, XRD, thermal decomposition and element analyses [6]. However, the thermochemical properties of the solid-state reaction at ambient temperature have not been reported. The purpose of the present study is to determine the dissolution enthalpies of the reactants and the products of the solid-state coordination reaction by solution calorimetry. The standard molar formation enthalpy of $[\text{Cu}(\text{HQ})\text{Cl}_2, \text{s}, 298.15 \text{ K}]$ has been derived from the respective dissolution enthalpy.

2. Experimental

2.1. Reagents

8-Hydroxyquinoline is abbreviated as HQ. All the chemicals ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 8-hydroxyquinoline and hydrochloric acid) used were of analytical grade.

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KCl, calorimetric primary standard of purity >99.99%, was dried in a vacuum oven for 6 h at 408 K prior to use. Doubly distilled water was used throughout the experiment.

2.2. Calorimeter

The isoperibol reaction calorimeter used for this study was made at laboratory of thermochemistry in Wuhan University and was adapted for measuring enthalpies of solid–liquid, liquid–liquid reaction [8,9]. The volume of the calorimetric cell is 100 ml. The accuracy of temperature maintenance and measurement are ± 0.001 and ± 0.0001 K, respectively.

The accuracy of the calorimeter was tested by measuring the dissolution enthalpy of THAM (NBS 742a, USA) in 0.1 mol l^{-1} HCl and the KCl (calorimetric primary standard) in twice distilled water at 298.15 K. The mean dissolution enthalpies are $-29\,7766 \pm 16 \text{ J mol}^{-1}$ for THAM and $17\,597 \pm 17 \text{ J mol}^{-1}$ for KCl, which are in good agreement with the respective published data [10,11].

2.3. Preparations

$\text{Cu}(\text{HQ})\text{Cl}_2(\text{s})$ was prepared by grinding a homogenized mixture of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 8-hydroxyquinoline (mole ratio is 1:1) at an agate mortar at room temperature according to the method of Xinquan Xin [7]. The product was put in a thermostat at 313 K until constant weight was obtained.

Table 1

Dissolution enthalpies of $\text{Cu}(\text{HQ})\text{Cl}_2(\text{s})$, $[\text{CuCl}_2 \cdot 2\text{H}_2\text{O}(\text{s}) + \text{HQ}(\text{s})]$ in 3 mol l^{-1} HCl at 298.15 K

System	No.	m^a (g)	$-Q^b$ (J)	$\Delta_s H_m^\ominus$ (kJ mol $^{-1}$)
$\Delta_s H_m^\ominus[\text{Cu}(\text{HQ})\text{Cl}_2(\text{s})] = -2.621 \pm 0.033 \text{ kJ mol}^{-1}$				
$\text{Cu}(\text{HQ})\text{Cl}_2(\text{s})$	–1	0.2089	1.941	2.598
	2	0.1987	1.837	2.586
	3	0.2103	1.959	2.605
	4	0.2063	1.954	2.648
	5	0.2053	1.964	2.670
$\Delta_s H_m^\ominus[\text{CuCl}_2 \cdot 2\text{H}_2\text{O}(\text{s}) + \text{HQ}(\text{s})] = -9.816 \pm 0.047 \text{ kJ mol}^{-1}$				
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}(\text{s}) + \text{HQ}(\text{s})$	1	0.1931	5.987	9.786
	2	0.2127	6.640	9.852
	3	0.1923	6.000	9.845
	4	0.2009	6.198	9.739
	5	0.1972	6.157	9.856

^a Mass of sample.

^b Heat effect.

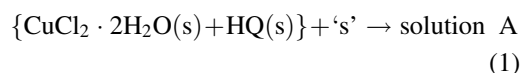
3. Results and discussion

3.1. The calorimetric solvent

In this experiment, 100 ml 3 mol l^{-1} HCl was chosen as calorimetric solvent to determine the dissolution enthalpies of the reactants ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and HQ), and the products ($\text{Cu}(\text{HQ})\text{Cl}_2$ and $2\text{H}_2\text{O}$) of the solid-state coordination reaction.

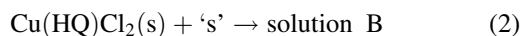
3.2. The standard molar formation enthalpy of $\text{Cu}(\text{HQ})\text{Cl}_2(\text{s})$

Samples of mass 0.20 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and HQ in a mole ratio 1:1 were dissolved in 100 ml 3 mol l^{-1} HCl at 298.15 K.



where 's' is calorimetric solvent.

The dissolution enthalpies of $\text{Cu}(\text{HQ})\text{Cl}_2(\text{s})$ in 3 mol l^{-1} HCl was measured under the same condition.



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

The dissolution enthalpy of the products $2\text{H}_2\text{O}$ in solution B lies below the sensitivity of the calorimeter not to measure accurately. Thus, it is ignored and does not affect the experimental result.

Table 2

Reaction scheme for the standard molar formation enthalpy of Cu(HQ)Cl₂(s) at the temperature 298.15 K^a

No.	Reaction	Solution	$\Delta_s H_m^\ominus$ (kJ mol ⁻¹)
1.	{CuCl ₂ ·2H ₂ O(s)+HQ(s)}+‘s’	A	-9.816±0.047
2.	Cu(HQ)Cl ₂ (s)+‘s’	B	-2.621±0.033
3.	9C(s)+1/2N ₂ (g)+7/2H ₂ (g)+1/2O ₂ (g)=HQ(s)		-83.26
4.	Cu(s)+Cl ₂ (g)+O ₂ (g)+2H ₂ (g)=CuCl ₂ ·2H ₂ O(s)		-821.32
5.	H ₂ (g)+1/2O ₂ (g)=H ₂ O(l)		-285.83
6.	Cu(s)+Cl ₂ (g)+1/2O ₂ (g)+1/2N ₂ (g)+7/2H ₂ (g)+9C(s) =Cu(HQ)Cl ₂ (s)		-340.12

^a The solvent ‘s’ was 3 mol l⁻¹ HCl. $\Delta H_6 = \Delta H_1 - \Delta H_2 + \Delta H_3 + \Delta H_4 - 2\Delta H_5$.

The reaction scheme used to derive the standard molar formation enthalpy of Cu(HQ)Cl₂(s) is given in Table 2. The molar dissolution enthalpy of CuCl₂·2H₂O and HQ mixture at mole ratio of $n(\text{CuCl}_2 \cdot 2\text{H}_2\text{O})/n(\text{HQ})=1:1$ was determined in 3 mol l⁻¹ HCl. In the same conditions, we have measured the molar dissolution enthalpy of Cu(HQ)Cl₂(s). These values were combined with auxiliary values of $\Delta_f H_m^\ominus = -821.32$ kJ mol⁻¹ for CuCl₂·2H₂O(s), -285.83 kJ mol⁻¹ for H₂O [12] and -83.26 kJ mol⁻¹ for HQ(s) [13] to derive the standard molar formation enthalpy of [Cu(HQ)Cl₂(s)]: $\Delta_f H_m^\ominus$ (Cu(HQ)Cl₂,s,298.15 K) = -340.12 kJ mol⁻¹.

In this paper, we confirm thermodynamic identity solutions A and B by UV spectroscopy and the data of the refractive index, and used the unique thermochemical cycle with calorimetric solvent for (Cu(HQ)Cl₂(s) and [CuCl₂·2H₂O(s)+HQ(s)]. Thus, we believe that $\Delta_f H_m^\ominus$ value determined by solution calorimetry measurement is reliable.

Acknowledgements

This work was supported by the National Natural Science Foundation of China and the Chinese Postdoctoral Science Foundation.

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