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A thermochemical study of the reaction of $CuCl_2 \cdot 2H_2O$ with 8-hydroxyquinoline

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Abstract

The solid-state coordination reaction of $CuCl_2 \cdot 2H_2O$ with 8-hydroxyquinoline (HQ): $HQ(s)+CuCl_2 \cdot 2H_2O(s) \rightarrow Cu(HQ)Cl_2(s)+2H_2O(l)$ has been studied by solution calorimetry. The molar dissolution enthalpies of the reactants and the products in $3\ \mathrm{mol\ l^{-1}}$ 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 [$Cu(HQ)Cl_2$,s,298.15 K] at 298.15 K has been derived: $\Delta_f H_m^\ominus(Cu(HQ)Cl_2,s,298.15\ K)=-340.12\ \mathrm{kJ\ mol^{-1}}$.

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 $CuCl_2 \cdot 2H_2O$ 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 [$Cu(HQ)Cl_2$,s,298.15 K] has been derived from the respective dissolution enthalpy.

2. Experimental

2.1. Reagents

8-Hydroxyquinoline is abbreviated as HQ. All the chemicals ($CuCl_2 \cdot 2H_2O$, 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 $-29\,7766\pm16$ J mol^{-1} for THAM and $17\,597\pm17$ J mol^{-1} for KCl, which are in good agreement with the respective published data [10,11].

2.3. Preparations

$Cu(HQ)Cl_2(s)$ was prepared by grinding a homogenized mixture of $CuCl_2\cdot2H_2O$ 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.

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 ($CuCl_2\cdot2H_2O$ and HQ), and the products ($Cu(HQ)Cl_2$ and $2H_2O$) of the solid-state coordination reaction.

3.2. The standard molar formation enthalpy of $Cu(HQ)Cl_2(s)$

Samples of mass 0.20 g of $CuCl_2\cdot2H_2O$ and HQ in a mole ratio 1:1 were dissolved in 100 ml 3 mol l^{-1} HCl at 298.15 K.

$$\{CuCl_2\cdot2H_2O(s)+HQ(s)\}+\text{`s'}\rightarrow \text{solution A} \tag{1}$$

where ‘s’ is calorimetric solvent.

The dissolution enthalpies of $Cu(HQ)Cl_2(s)$ in 3 mol l^{-1} HCl was measured under the same condition.

$$Cu(HQ)Cl_2(s)+\text{`s'}\rightarrow \text{solution B} \tag{2}$$

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

The dissolution enthalpy of the products $2H_2O$ 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 1
Dissolution enthalpies of $Cu(HQ)Cl_2(s)$, $[CuCl_2\cdot2H_2O(s)+HQ(s)]$ in 3 mol l^{-1} HCl at 298.15 K

System	No.	m^a (g)	$-Q^b$ (J)	$\Delta_sH_m^{\ominus}$ (kJ mol^{-1})
$\Delta_sH_m^{\ominus}[Cu(HQ)Cl_2(s)]=-2.621\pm0.033$ kJ mol^{-1}				
$Cu(HQ)Cl_2(s)$	−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
$\Delta_sH_m^{\ominus}[CuCl_2\cdot2H_2O(s)+HQ(s)]=-9.816\pm0.047$ kJ mol^{-1}				
$CuCl_2\cdot2H_2O(s)+HQ(s)$	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.

Table 2
Reaction scheme for the standard molar formation enthalpy of $Cu(HQ)Cl_2(s)$ at the temperature 298.15 K[a]

No.	Reaction	Solution	$\Delta_s H_m^\ominus$ (kJ mol^{-1})
1.	$\{CuCl_2{\cdot}2H_2O(s)+HQ(s)\}+$'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.	$Cu(s)+Cl_2(g)+O_2(g)+2H_2(g)=CuCl_2{\cdot}2H_2O(s)$		-821.32
5.	$H_2(g)+1/2O_2(g)=H_2O(l)$		-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 $Cu(HQ)Cl_2(s)$ is given in Table 2. The molar dissolution enthalpy of $CuCl_2{\cdot}2H_2O$ and HQ mixture at mole ratio of $n(CuCl_2{\cdot}2H_2O)/n(HQ)=1{:}1$ was determined in 3 mol l^{-1} HCl. In the same conditions, we have measured the molar dissolution enthalpy of $Cu(HQ)Cl_2(s)$. These values were combined with auxiliary values of $\Delta_f H_m^\ominus=-821.32$ kJ mol^{-1} for $CuCl_2{\cdot}2H_2O(s)$, -285.83 kJ mol^{-1} for H_2O [12] and -83.26 kJ mol^{-1} for HQ(s) [13] to derive the standard molar formation enthalpy of $[Cu(HQ)Cl_2(s)]$: $\Delta_f H_m^\ominus$ $(Cu(HQ)Cl_2$,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 $(Cu(HQ)Cl_2(s)$ and $[CuCl_2{\cdot}2H_2O(s)+HQ(s)]$. Thus, we believe that $\Delta_f H_m^\ominus$ value determined by solution calorimetry measurement is reliable.

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References

[1] N.B. Singh, R.P. Singh, J Solid State Chem. 33 (1980) 391.

[2] M.B. Beg, A. Ahamad, H. Askari, J. Solid State Chem. 68 (1987) 22.

[3] P.S. Bassi, G.S. Chopra, K. Kaur, Indian J Chem. 29A (1990) 454.

[4] DianZeng Jia, Changxiong Li, Yan Fu, Xingquan Xin, Acta Chem. Sinica 51 (1993) 363.

[5] B.L. Bubey, N. Tiwari, Indian J Chem. 30A (1991) 855.

[6] Lixu Lei, Xingquan Xin, Thermochim. Acta 273 (1996) 61.

[7] A. Burger, Medical Chemistry, 3rd Edition, Wiley-Interscience, London, 1970, 635 pp.

[8] C.X. Wang, Z.H. Song, W.G. Xiong, S.S. Qu, Acta Physico-Chimica Sinica 7 (5) (1991) 586.

[9] T.Z. Wang, Y. Yu, Y. Liu, P.J. Zhou, S.S. Qu, Thermochim. Acta 333 (1999) 1.

[10] R. Rychly, V. Pekarek, J. Chem. Thermodyn. 9 (1977) 391.

[11] R.L. Montgomery, R.A. Melaugh, C.C. Lau, G.H. Meier, H.H. Chan, F.D. Rossini, J. Chem. Thermodyn. 9 (1977) 915.

[12] D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I.B. Halow, S.M. Bailey, K.L. Churney, R.L. Nuttall, The NBS tables of Chemical Thermodynamic Properties, J. Phys. Chem. Ref. Data (Suppl. 2) 11 (1982).

[13] J.A. Dean, Lange's Handbook of Chemistry, 13th Edition, McGraw-Hill, New York, 1985.