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Short communication

A thermochemical study on the coordination complex of cerium trichloroacetic acid with 8-hydroxyquinoline

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Abstract

The standard molar reaction enthalpies of two reactions, $CeCl_3{\cdot}7H_2O(s) + 3CCl_3COOH(s)(\text{or TCA}) = Ce(TCA)_3{\cdot}3H_2O(s) + 3HCl(g) + 4H_2O(l)$ and $Ce(TCA)_3{\cdot}3H_2O(s) + 2C_9H_7NO(s) = Ce(TCA)(C_9H_6NO)_2(s) + 2CCl_3COOH(s) + 3H_2O(l)$, were studied by classical solution calorimetry at 298.15 K. The molar dissolution enthalpies of the reactants and the products in certain solvent (the first reaction in 1 mol/l HCl, the second in a mixed solution consisting of absolute ethyl alcohol, dimethyl sulfoxide and 4 mol/l HCl) have been measured by using an isoperibolic calorimeter at 298.15 K. From the results and other auxiliary quantities, the standard molar formation enthalpies of [$Ce(TCA)_3{\cdot}3H_2O$, s, 298.15 K] and [$Ce(TCA)(C_9H_6NO)_2$, s, 298.15 K] were determined to be $\Delta_f H_m^\theta$ [$Ce(TCA)_3{\cdot}3H_2O$, s, 298.15 K] = −3059.9 kJ/mol and $\Delta_f H_m^\theta$ [$Ce(TCA)(C_9H_6NO)_2$, s, 298.15 K] = −1368.9 kJ/mol.

Keywords: Cerium chloride seven-hydrate; Trichloroacetic acid; 8-Hydroxyquinoline; Thermochemical; Formation enthalpy

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1. Introduction

Both rare earth ions [1] and 8-hydroxyquinoline are of antibacterial function [2], and their complexes have more powerful disinfection effects. Their binary complexes were reported as early as 1963. The research on their ternary complexes has increased in recent years in many fields [3–6]. Dong and Zhu reported the synthesis and characterization of the complexes of rare earth trichloroacetic acid salts with 8-hydroxyquinoline [6]. Its application in leather mouldyproof showed that the complexes have powerful disinfection effects. Obviously, it is very important to study the complexes of rare earth trichloroacetic acid salts and 8-hydroxyquinoline. Therefore, it is necessary to obtain their basic thermodynamic data. However, the thermodynamic properties of the complexes have not been reported. In this paper, using a new type of isoperibolic reaction calorimeter [7], we determined the dissolution enthalpies of $CeCl_3{\cdot}7H_2O(s)$, $CCl_3COOH(s)$ and $Ce(TCA)_3{\cdot}3H_2O(s)$ in 1 mol/l HCl. Using Hess' law, we obtained the reaction enthalpy of the reaction (1),

$$\begin{aligned} &CeCl_3\cdot 7H_2O(s) + 3CCl_3COOH(s)(\text{or TCA}) \\ &\quad = Ce(TCA)_3\cdot 3H_2O(s) + 3HCl(g) + 4H_2O(l) \end{aligned} \tag{1}$$

and estimated the standard formation enthalpy of $Ce(TCA)_3{\cdot}3H_2O(s)$. We also determined the dissolution enthalpies of $Ce(TCA)_3{\cdot}3H_2O(s)$, $C_9H_7NO(s)$,

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$Ce(TCA)(C_9H_6NO)_2(s)$ and $CCl_3COOH(s)$ in a solution of absolute ethyl alcohol, dimethyl sulfoxide and 4 mol/l HCl. The reaction enthalpy of the reaction (1′)

$$\begin{aligned}&Ce(TCA)_3 \cdot 3H_2O(s) + 2C_9H_7NO(s)\\&\quad = Ce(TCA)(C_9H_6NO)_2(s) + 2CCl_3COOH(s)\\&\qquad +3H_2O(l) \qquad (1')\end{aligned}$$

was calculated and the standard formation enthalpy of $Ce(TCA)(C_9H_6NO)_2(s)$ was estimated.

2. Experimental

2.1. Chemicals

The chemicals $CeCl_3 \cdot 7H_2O(s)$, $CCl_3COOH(s)$, $C_9H_7NO(s)$ and KCl used were of A. R. grade and obtained from Shanghai Reagent Company.

$CeCl_3 \cdot 7H_2O(s)$, with a purity >99%, was dried prior to use in a desiccator containing sulphuric acid of 60% [8] at room temperature to constant mass; $CCl_3COOH(s)$ with a purity >99.5% was dried prior to use in a vacuum desiccator containing P_4O_{10} until constant mass; KCl (calorimetric primary standard) of purity >99.99%, was dried in a vacuum oven for 6 h at 135 °C prior to use; $C_9H_7NO(s)$(8-hydroxyquinoline) with a purity >99.5% was used.

2.2. Preparations

$Ce(TCA)_3 \cdot 3H_2O(s)$ was prepared according to the method given in [6]. Crystals were obtained by repeated crystallization in a mixed solution consisting of C_2H_5OH and $CHCl_3$. Then the product was put into a desiccator containing P_4O_{10} until the mass of the crystal was constant. The chemical analysis proved that the composition of the complex was $Ce(TCA)_3 \cdot 3H_2O(s)$, the purity was >99.5%.

$Ce(TCA)(C_9H_6NO)_2(s)$, a yellow solid, was prepared and analyzed according to the method given in [6].

2.3. Calorimeter and calibration

The isoperibolic reaction calorimeter was constructed in this laboratory and was adapted to determine the enthalpies of solid–solid and liquid–liquid reaction [7]. The volume of the reaction vessel was 100 cm^3. The precision of temperature control and measurement were ±0.001 and ±0.0001 K, respectively.

The calorimeter was tested by measuring the dissolution enthalpies of KCl (calorimetric primary standard) in water at 298.15 K. The mean dissolution enthalpies was 17597 ± 17 J/mol, which is in agreement with the reported data 17536 ± 9 J/mol for KCl [9]. The uncertainty are <0.4% that proves that the calorimeter is reliable.

2.4. Determination of dissolution enthalpies

The method was the same as that for the calibration of the calorimeter with KCl. All samples were dissolved in 100 cm^3 1 mol/l HCl solution.

2.4.1. Determination of $\Delta_s H_m^\theta$ [$CeCl_3 \cdot 7H_2O(s)$]

$CeCl_3 \cdot 7H_2O(s)$ was powdered in an agate bowl and 0.372 g $CeCl_3 \cdot 7H_2O(s)$ were put into the cell of calorimeter. 100 cm^3 1 mol/l HCl were put into the reaction vessel. The calorimeter was brought to constant temperature, and then the dissolution enthalpy was determined. The determination was repeated for five times. The experimental results are shown in Table 1.

2.4.2. Determination of $\Delta_s H_m^\theta$ [$3CCl_3COOH(s)$]

The solution in Section 2.4.1 was kept in the reaction vessel, then powdered 0.49 g $CCl_3COOH(s)$ were put into calorimetric cell. The dissolution enthalpies were determined for five times. Experimental results are shown in Table 1.

2.4.3. Determination of $\Delta_s H_m^\theta$ [$Ce(TCA)_3 \cdot 3H_2O(s)$]

Powdered $Ce(TCA)_3 \cdot 3H_2O(s)$ (0.68 g) were put into sampling cell of calorimeter, 100 cm^3 1 mol/l HCl were put into the reaction vessel. The calorimeter was brought to constant temperature. The determination was repeated for five times. The results are shown in Table 1.

2.5. Determination of dissolution enthalpies of materials in reaction (1′)

The method of determination of dissolution enthalpies of the samples is the same as that for the

Table 1
Dissolution enthalpies of [$CeCl_3 \cdot 7H_2O(s)$], [$3CCl_3COOH(s)$] and [$Ce(TCA)_3 \cdot 3H_2O(s)$] in 1 mol/l HCl (at 298.15 K, $R = 1003.6\,\Omega$, $I = 20.123$ mA)

System	No.	n ($\times 10^{-3}$ mol)	ΔE_s (mV)	ΔE_e (mV)	t/s	Q_s (J)	$\Delta_s H_m^\theta$ (kJ/mol)
A	1	1.0165	5.2037	5.2919	128.53	51.364	50.530
	2	1.0205	5.2285	5.3113	129.00	51.609	50.572
	3	1.0001	5.1356	5.3565	130.10	50.692	50.687
	4	1.0085	5.1741	5.3627	130.25	51.072	50.641
	5	1.0130	5.1973	5.3524	130.00	51.301	50.643
$\Delta_s H_m^\theta(2) = \Delta_s H_m^\theta[CeCl_3 \cdot 7H_2O, s, 298.15\,K] = 50.62 \pm 0.03$ kJ/mol							
B	1	1.0091	2.2758	2.4033	61.33	23.602	23.388
	2	1.0129	2.2929	2.4483	62.50	23.788	23.484
	3	1.0068	2.2757	2.2638	57.77	23.601	23.441
	4	1.0018	2.2559	2.4727	63.10	23.395	23.352
	5	1.0052	2.2769	2.4100	61.50	23.613	23.490
$\Delta_s H_m^\theta(3) = \Delta_s H_m^\theta[3CCl_3COOH, s, 298.15\,K] = 23.43 \pm 0.03$ kJ/mol							
C	1	0.9976	9.3631	9.3421	230.67	93.955	94.181
	2	1.0030	9.4187	9.3476	230.80	94.511	94.228
	3	0.9985	9.3720	9.3555	231.00	94.044	94.185
	4	1.0012	9.4004	9.3191	230.10	94.328	94.215
	5	1.0022	9.4104	9.3373	230.55	94.429	94.222
$\Delta_s H_m^\theta(4) = \Delta_s H_m^\theta[Ce(TCA) \cdot 3H_2O, s, 298.15\,K] = 94.21 \pm 0.01$ kJ/mol							

n, mole of sample; t, heating period of electrical calibration; Q_s, heat effect; ΔE_s, the voltage change during the sample dissolution; ΔE_e, the voltage change during the electrical calibration. $\Delta_s H_m^\theta = (\Delta E_s/\Delta E_e) I^2 Rt(1/n)$ where R is the resistance; I, the current; A, the solution of $CeCl_3 \cdot 7H_2O(s)$ in 1 mol/l HCl; B, the solution of $3CCl_3COOH(s)$ in A; C, the solution of $Ce(TCA)_3 \cdot 3H_2O(s)$ in 1 mol/l HCl.

calibration of the calorimeter with KCl. All were dissolved in 100 cm^3 mixed solution of dimethyl sulfoxide and absolute ethyl alcohol and 4 mol/l HCl.

2.5.1. Choice of solvent

Cerium trichloroacetic acid and 8-hydroxyquinoline complex can not be dissoluted in a single solvent. We examined many of common solvents and solvents mixed in different proportion, and finally discovered that a mixture of dimethyl sulfoxide and absolute ethyl alcohol and 4 mol/l HCl ($V_{HCl} : V_{EtOH} : V_{DMSO} = 1 : 0.5 : 0.5$) is the most appropriate solvent. The experiment was done in it (B* represented the solution).

2.5.2. Determination of $\Delta_s H_m^\theta$ [$Ce(TCA)_3 \cdot 3H_2O(s)$]

$Ce(TCA)_3 \cdot 3H_2O(s)$ was powdered in an agate bowl. 0.68 g sample were put into sampling cell of calorimeter. 100 cm^3 B* were put into the reaction vessel (A′ represented the solution). The calorimeter was brought to constant temperature, and the determination was repeated for five times. Experimental results are shown in Table 2.

2.5.3. Determination of $\Delta_s H_m^\theta$ [$2C_9H_7NO(s)$]

Powdered $C_9H_7NO(s)$ (0.29 g) was put into the sampling cell. Then the solution A′ of Section 2.5.2 was kept in the reaction vessel (B′ represented the solution). The determination of the dissolution enthalpy was repeated for five times. Experimental results are shown in Table 2.

2.5.4. Determination of $\Delta_s H_m^\theta$ [$Ce(TCA)(C_9H_6NO)_2(s)$]

Powdered $Ce(TCA)(C_9H_6NO)_2(s)$ (0.59 g) was put into the sampling cell of the calorimeter. 100 cm^3 of the solution B* was put into the reaction vessel (C′ represented the solution). The calorimeter was brought to constant temperature. The determination was repeated for five times. Experimental results are shown in Table 2.

2.5.5. Determination of $\Delta_s H_m^\theta$ [$2CCl_3COOH(s)$]

Powdered $CCl_3COOH(s)$ (0.32 g) was put into the sampling cell. The solution C′ of Section 2.5.4 was kept in the reaction vessel (D′ represented the solu-

Table 2
Dissolution enthalpies of [Ce(TCA)$_3$·3H$_2$O(s)], [2C$_9$H$_7$NO(s)], [Ce(TCA)(C$_9$H$_6$NO)$_2$(s)] and 2CCl$_3$COOH(s)] in a mixed solvent B* (at 298.15 K, $R = 1003.6\,\Omega$, $I = 20.123$ mA)

System	No.	n ($\times 10^{-3}$ mol)	ΔE_s (mV)	ΔE_e (mV)	t/s	Q_s (J)	$\Delta_s H_m^\theta$ (kJ/mol)
A′	1	1.0022	8.5642	8.4929	132.50	54.300	54.181
	2	1.0003	8.5381	8.3313	129.98	54.135	54.119
	3	1.0025	8.5635	8.4608	132.00	54.296	54.161
	4	0.9994	8.5436	8.3326	130.00	54.170	54.202
	5	1.0028	8.5555	8.4993	132.60	54.245	54.094
$\Delta_s H_m^\theta(2') = \Delta_s H_m^\theta$[Ce(TCA)$_3$·3H$_2$O, s, 298.15 K] = 54.15 ± 0.02 kJ/mol							
B′	1	1.0068	4.3632	4.0024	62.60	27.734	27.547
	2	1.0010	4.3419	3.9832	62.30	27.599	27.571
	3	1.0030	4.3431	3.9967	62.51	27.606	27.523
	4	0.9968	4.3076	3.9641	62.00	27.380	27.468
	5	1.0030	4.3107	3.9960	62.50	27.400	27.318
$\Delta_s H_m^\theta(3') = \Delta_s H_m^\theta$[2C$_9H_7$NO, s, 298.15 K] = 27.49 ± 0.05 kJ/mol							
C′	1	1.0015	11.8075	11.6511	259.08	106.703	106.543
	2	0.9930	11.6973	11.7091	260.37	105.708	106.453
	3	1.0001	11.7539	11.7581	261.46	106.219	103.208
	4	0.9865	11.6208	11.6700	259.50	105.016	106.453
	5	0.9970	11.8385	11.7158	260.52	106.984	106.303
(4′) = $\Delta_s H_m^\theta$[Ce(TCA)(C$_9$H$_6$NO)$_2$, s, 298.15 K] = 106.39 ± 0.06 kJ/mol							
D′	1	1.0052	2.4522	2.3295	35.00	−14.973	−14.896
	2	1.0006	2.4222	2.3043	34.65	−14.802	−14.793
	3	1.0014	2.4514	2.3375	35.12	−14.968	−14.947
	4	1.0019	2.4485	2.3429	35.20	−14.950	−14.922
	5	1.0058	2.4558	2.3362	35.10	−14.995	−14.908
$\Delta_s H_m^\theta(5') = \Delta_s H_m^\theta$[2CCl$_3$COOH, s, 298.15 K] = −14.89 ± 0.03 kJ/mol							

tion). The determination was repeated for five times. Experimental results are shown in Table 2.

3. Results and discussion

3.1. Reaction (1)

3.1.1. Thermochemical cycle of the reaction (1)

According to Hess’ law, a thermochemical cycle was designed as shown in Table 3.

3.1.2. Evaluation of the standard molar formation enthalpy of Ce(TCA)$_3$·3H$_2$O(s)

According to the thermochemical cycle in Table 3, the standard reaction enthalpy is

$$\Delta_r H_m^\theta(1) = \Delta_s H_m^\theta(2) + \Delta_s H_m^\theta(3) - \Delta_s H_m^\theta(4) - \Delta_s H_m^\theta(5) - \Delta_s H_m^\theta(6)$$

According to Table 3,

$$\Delta_r H_m^\theta(1) = 204.28\,\mathrm{kJ/mol}$$

According to thermodynamics principle, we know that

$$\begin{aligned}\Delta_r H_m^\theta(1) = {} & \Delta_f H_m^\theta[\mathrm{Ce(TCA)_3\cdot 3H_2O, s, 298.15\,K}] \\ & + 3\Delta_f H_m^\theta[\mathrm{HCl, g, 298.15\,K}] \\ & + 4\Delta_f H_m^\theta[\mathrm{H_2O, l, 298.15\,K}] \\ & - \Delta_f H_m^\theta[\mathrm{CeCl_3\cdot 7H_2O, s, 298.15\,K}] \\ & - 3\Delta_f H_m^\theta[\mathrm{CCl_3COOH, s, 298.15\,K}]\end{aligned}$$

According to [11],

$$\Delta_f H_m^\theta[\mathrm{HCl, g, 298.15\,K}] = -92.307\,\mathrm{kJ/mol}$$

$$\Delta_f H_m^\theta[\mathrm{H_2O, l, 298.15\,K}] = -285.830\,\mathrm{kJ/mol}$$

$$\Delta_f H_m^\theta[\mathrm{CeCl_3\cdot 7H_2O, s, 298.15\,K}] = -3169.4\,\mathrm{kJ/mol}$$

$$\Delta_f H_m^\theta[\mathrm{CCl_3COOH, s, 298.15\,K}] = -505.0\,\mathrm{kJ/mol}$$

Table 3
The reaction scheme for the standard molar reaction enthalpy of [$CeCl_3{\cdot}7H_2O(s) + 3CCl_3COOH(s)$] at 298.15 K

	Reactions	$\Delta_r H_m^\theta$ (kJ/mol)
(1)	$CeCl_3 \cdot 7H_2O(s) + 3CCl_3COOH(s) = Ce(TCA)_3 \cdot 3H_2O(s) + 3HCl(g) + 4H_2O(l)$	204.28
(2)	$CeCl_3 \cdot 7H_2O(s) + Sln = CeCl_3 \cdot 7H_2O(in\ Sln)$	50.62
(3)	$3CCl_3COOH(s) + CeCl_3 \cdot 7H_2O\ (in\ Sln) = 3CCl_3COOH \cdot CeCl_3 \cdot 7H_2O\ (in\ Sln)$	23.43
(4)	$Ce(TCA)_3 \cdot 3H_2O(s) + Sln = Ce \cdot 3TCA^- \cdot 3H_2O\ (in\ Sln)$	94.21
(5)	$3HCl(g) + Ce \cdot 3TCA^- \cdot 3H_2O\ (in\ Sln) = 3CCl_3COOH \cdot CeCl_3 \cdot 3H_2O\ (in\ Sln)$	−224.439
(6)	$4H_2O(l) + 3CCl_3COOH \cdot CeCl_3 \cdot 3H_2O\ (in\ Sln) = 3CCl_3COOH \cdot CeCl_3 \cdot$ $7H_2O\ (in\ Sln)_4H_2O(l) + 3CCl_3COOH \cdot CeCl_3 \cdot 3H_2O\ (in\ Sln) =$ $3CCl_3COOH \cdot CeCl_3 \times 7H_2O\ (in\ Sln)$	0

The solvent Sln was 1 mol/l HCl.

and the above-mentioned values

$$\Delta_r H_m^\theta(1) = 204.28\ \text{kJ/mol}$$

so that

$$\Delta_f H_m^\theta[Ce(TCA)_3 \cdot 3H_2O,\ s,\ 298.15\ K] = -3059.9\ \text{kJ/mol}$$

3.1.3. Discussion

3.1.3.1. Determination of dissolution with Japanese UV-160 UV spectrograph and WZS-1 refractometer. We determined the spectra and refractive indexes of dissolution products of [$CeCl_3{\cdot}7H_2O(s) + 3CCl_3COOH(s)$] and [$Ce(TCA){\cdot}3H_2O(s) + 3HCl(g) + 4H_2O(l)$] in 1 mol/l HCl, and discovered that their UV spectra are identical and that their refractive indexes are equal ($\eta_{25\,^\circ C} = 1.3431$). It proves that both dissolution products have the same thermodynamics state and thermochemical cycle of the reaction (1) is correct.

3.1.3.2. Treatment of $\Delta_s H_m^\theta(5)$. According to the relationship of integral enthalpies of dilution with integral enthalpies of two solutions with different concentration before and after dilution [10], we obtain

$$\Delta_d H_m^\theta = \Delta_s H_m^\theta(\text{dilute}) - \Delta_s H_m^\theta(\text{concentrated})$$

so that

$$\Delta_s H_m^\theta(m = 1.030\ \text{mol/l}) = \Delta_s H_m^\theta(m = 1.000\ \text{mol/l}) - \Delta_d H^\theta(1.030 \rightarrow 1.000)$$

According to [11],

$$\Delta_s H_\infty^\theta(\text{HCl, g, 298.15 K}) = -17,888\ \text{cal/mol} = -74.843\ \text{kJ/mol}$$

According to the relationship between infinitely dilute integral enthalpy of dilution with relatively apparent molar enthalpy [12]

$$\Delta_d H_{m\rightarrow 0}^\theta = -\Phi_{L2}$$

According to the data in [11],

$$\begin{aligned}\Delta_d H_{(1.030\rightarrow 1.000)}^\theta &= \Delta_d H_{(1.030\rightarrow 0)}^\theta - \Delta_d H_{(1.000\rightarrow 0)}^\theta \\ &= -\Phi_{L(1.030)} - [-\Phi_{L(1.000)}] \\ &= [-1.72 - (-1.69)]\ \text{kJ/mol} = -0.03\ \text{kJ/mol}\end{aligned}$$

so that

$$\begin{aligned}\Delta_s H_m^\theta(m = 1.030\ \text{mol/l}) &= \Delta_s H_m^\theta(m = 1.000\ \text{mol/l}) - \Delta_d H_{(1.030\rightarrow 1.000)}^\theta \\ &= [-74.843-(-0.03)]\ \text{kJ/mol} = -74.813\ \text{kJ/mol}\end{aligned}$$

and

$$\begin{aligned}\Delta_s H_m^\theta(5) &= 3 \times \Delta_s H_m^\theta(m = 1\ \text{mol/l}) \\ &= 3 \times (-74.813\ \text{kJ/mol}) = -224.439\ \text{kJ/mol}\end{aligned}$$

3.1.4. Treatment of $\Delta_s H_m^\theta(6)$

Because of the low concentration of $CeCl_3$ and $3CCl_3COOH$ in solution C, the dilution enthalpies of $CeCl_3$ and $3CCl_3COOH$ are small when "$4H_2O$" are added to the solution. The same is valid when "$4H_2O$" are added to 1 mol/l HCl. Therefore, these dilution enthalpies can be neglected, so that $\Delta_s H_m^\theta(6) \approx 0$.

Table 4
The reaction scheme for the standard molar reaction enthalpy of [Ce(TCA)$_3$·3H$_2$O(s) +2C$_9$H$_7$NO(s)] at 298.15 K

	Reactions	$\Delta_s H_m^\theta$ (kJ/mol)
(1′)	$\mathrm{Ce(TCA)_3 \cdot 3H_2O(s) + 2C_9H_7NO(s) = Ce(TCA)(C_9H_6NO)_2(s) + 2CCl_3COOH(s) + 3H_2O(l)}$	−9.86
(2′)	$\mathrm{[Ce(TCA)_3 \cdot 3H_2O(s)] + B^* = [Ce \cdot 3TCA \cdot 3H_2O](in\,B^*)}$	54.15
(3′)	$\mathrm{2C_9H_7NO(s) + [Ce \cdot 3TCA \cdot 3H_2O](in\,B^*) = [Ce \cdot 3TCA \cdot 2C_9H_6NO \cdot 3H_2O](in\,B^*)}$	27.49
(4′)	$\mathrm{Ce(TCA)(C_9H_6NO)_2(s) + B^* = [Ce \cdot TCA \cdot 2C_9H_6NO]\ (in\,B^*)}$	106.39
(5′)	$\mathrm{2CCl_3COOH(s) + [Ce \cdot TCA \cdot 2C_9H_6NO]\ (in\,B^*) = [Ce \cdot 3TCA \cdot 2C_9H_6NO]\ (in\,B^*)}$	−14.89
(6′)	$\mathrm{3H_2O(l) + [Ce \cdot 3TCA \cdot 2C_9H_6NO]\ (in\,B^*) = [Ce \cdot 3TCA \cdot 2C_9H_6NO \cdot 3H_2O]\ (in\,B^*)}$	0

3.2. Reaction (1′)

3.2.1. Thermochemical cycle of reaction (1′)

According to Hess' law, a thermochemical cycle was designed as shown in Table 4.

3.2.2. Evaluation of the standard molar formation enthalpy of Ce(TCA)(C$_9$H$_6$NO)$_2$(s)

According to the thermochemical cycle, the standard reaction enthalpy is

$$\begin{aligned}\Delta_r H_m^\theta(1') &= \Delta_s H_m^\theta(2') + \Delta_s H_m^\theta(3') - \Delta_s H_m^\theta(4') \\ &\quad - \Delta_s H_m^\theta(5') - \Delta_s H_m^\theta(6') = -9.86\,\mathrm{kJ/mol}\end{aligned}$$

According to thermodynamics principle, we know that

$$\begin{aligned}&\Delta_r H_m^\theta(1') \\ &= \Delta_f H_m^\theta[\mathrm{Ce(TCA)(C_9H_6NO)_2, s, 298.15\,K}] \\ &\quad + 2\Delta_f H_m^\theta[\mathrm{CCl_3COOH, s, 298.15\,K}] \\ &\quad + 3\Delta_f H_m^\theta[\mathrm{H_2O, l, 298.15\,K}] \\ &\quad - \Delta_f H_m^\theta[\mathrm{Ce(TCA)_3 \cdot 3H_2O, s, 298.15\,K}] \\ &\quad - 2\Delta_f H_m^\theta[\mathrm{C_9H_7NO, s, 298.15\,K}]\end{aligned}$$

According to [13]

$$\Delta_f H_m^\theta[\mathrm{C_9H_7NO, s, 298.15\,K}] = -83.3\,\mathrm{kJ/mol}$$

and with the above-mentioned values

$$\Delta_f H_m^\theta[\mathrm{CCl_3COOH, s, 298.15\,K}] = -505.0\,\mathrm{kJ/mol}$$

$$\begin{aligned}&\Delta_f H_m^\theta[\mathrm{Ce(TCA)_3 \cdot 3H_2O, s, 298.15\,K}] \\ &= -3059.9\,\mathrm{kJ/mol}\end{aligned}$$

$$\Delta_f H_m^\theta[\mathrm{H_2O, l, 298.15\,K}] = -285.830\,\mathrm{kJ/mol}$$

$$\Delta_r H_m^\theta(1') = -9.86\,\mathrm{kJ/mol}$$

so that

$$\begin{aligned}&\Delta_f H_m^\theta[\mathrm{Ce(TCA)(C_9H_6NO)_2, s, 298.15\,K}] \\ &= -1368.9\,\mathrm{kJ/mol}\end{aligned}$$

3.2.3. Discussion of the reaction (1′)

3.2.3.1. Determination of dissolution products with Japanese UV-160 UV spectrograph and WZS-1 refractometer. We determined the spectra and refraction indexes of the dissolution products of [CeTCA)$_3$· 3H$_2$O(s) + 2C$_9$H$_7$NO(s)] and [Ce(TCA)(C$_9$H$_6$NO)$_2$(s) + 2CCl$_3$COOH(s) + 3H$_2$O(l)] in solution B*. Their UV spectrums are identical and their refraction indexes are equal ($\eta_{25\,^\circ\mathrm{C}} = 1.4000$), therefore, both dissolution products have the same thermodynamics state and thermochemical cycle of the reaction (1′) is correct.

3.2.3.2. Treatment of $\Delta_s H_m^\theta(6')$. Because of small concentration of Ce(TCA)(C$_9$H$_6$NO)$_2$ and CCl$_3$COOH in the solution D' when "3H$_2$O" is put in, the dilution enthalpies can be neglected, so that $\Delta_s H_m^\theta(6') \approx 0$.

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