

THERMOCHEMISTRY OF THE SOLID COMPLEX $\text{Gd}(\text{Et}_2\text{dtc})_3(\text{phen})$

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A ternary solid complex $\text{Gd}(\text{Et}_2\text{dtc})_3(\text{phen})$ has been obtained from the reaction of sodium diethyldithiocarbamate (NaEt_2dtc), 1,10-phenanthroline (*phen*) and hydrated gadolinium chloride in absolute ethanol. The title complex was described by chemical and elemental analyses, TG-DTG and IR spectrum. The enthalpy change of liquid-phase reaction of formation of the complex, $\Delta_r H_m^\circ(l)$, was determined as $(-11.628 \pm 0.0204) \text{ kJ mol}^{-1}$ at 298.15 K by an RD-496 III heat conduction microcalorimeter. The enthalpy change of the solid-phase reaction of formation of the complex, $\Delta_r H_m^\circ(s)$, was calculated as $(145.306 \pm 0.519) \text{ kJ mol}^{-1}$ on the basis of a designed thermochemical cycle. The thermodynamics of reaction of formation of the complex was investigated by changing the temperature of liquid-phase reaction. Fundamental parameters, the apparent reaction rate constant (k), the apparent activation energy (E), the pre-exponential constant (A), the reaction order (n), the activation enthalpy (ΔH_\ddagger°), the activation entropy (ΔS_\ddagger°), the activation free energy (ΔG_\ddagger°) and the enthalpy ($\Delta_r H_\ddagger^\circ$), were obtained by combination of the thermodynamic and kinetic equations for the reaction with the data of thermokinetic experiments. The constant-volume combustion energy of the complex, $\Delta_c U$, was determined as $(-18673.71 \pm 8.15) \text{ kJ mol}^{-1}$ by an RBC-II rotating-bomb calorimeter at 298.15 K. Its standard enthalpy of combustion, $\Delta_c H_m^\circ$, and standard enthalpy of formation, $\Delta_f H_m^\circ$, were calculated to be $(-18692.92 \pm 8.15) \text{ kJ mol}^{-1}$ and $(-51.28 \pm 9.17) \text{ kJ mol}^{-1}$, respectively.

Keywords: constant-volume combustion energy, $\text{Gd}(\text{Et}_2\text{dtc})_3(\text{phen})$, microcalorimeter, standard enthalpy of formation, thermodynamic

Introduction

The prospect of generating new materials used for the precursors of ceramics and film [1–4] provides significant motivation for the research interest in coordination compounds containing lanthanide-sulfur bonds. Many investigations on the preparations, characterizations and structures of these kinds of compounds have been documented [5–7]. As part of our interests in the thermochemistry of complexes containing lanthanide-sulfur bonds, we have recently finished thermodynamic studies of reactions of rare earths with diethyldithiocarbamate [8], which is of great importance for understanding the driving forces in the coordination reaction systems and the energetics associated with the reaction processes in the formation of coordination compounds.

Calorimetry is a universal technique widely used for the measurements of enthalpies of reaction, dissolution, dilution, mixing, adsorption, formation, and excess enthalpies in a thermochemistry laboratory, which are involved in physical changes, chemical reactions and living biochemical metabolisms evidently in the nature. Especially calorimetry is often applied to determine the enthalpy change of many important chemical and physical processes in industrial and scientific research fields based on the data of enthalpies of dissolution or reaction and some auxiliary thermodynamic

quantities. The datum of the standard molar enthalpy of formation plays an important role in theoretical study, application development and industrial production of a compound as a basis of theoretical analysis. In spite of that, to our best knowledge, there is little reliable experimental data available for these complexes containing lanthanide-sulfur bonds.

In the present study, a novel ternary solid complex $\text{Gd}(\text{Et}_2\text{dtc})_3(\text{phen})$ has been synthesized from the reactions of gadolinium chloride hydrate with sodium diethyldithiocarbamate (NaEt_2dtc) and 1,10-phenanthroline (*phen*) in absolute ethanol. The complex was characterized by chemical and elemental analyses, TG-DTG and IR technique. The enthalpy change of the liquid-phase reaction $\Delta_r H_m^\circ(l)$ at 298.15 K was measured by an RD-496 III heat conduction microcalorimeter and that of solid-phase $\Delta_r H_m^\circ(s)$ was derived from a thermochemical cycle. The thermodynamics of the liquid-phase reaction at different temperatures were investigated, and fundamental parameters, the apparent reaction rate constant (k), the apparent activation energy (E), the pre-exponential constant (A), the reaction order (n), the activation enthalpy (ΔH_\ddagger°), the activation entropy (ΔS_\ddagger°), the activation free energy (ΔG_\ddagger°) and the enthalpy ($\Delta_r H_\ddagger^\circ$), were obtained on the basis of reaction thermodynamic and kinetic equations. The constant-volume combustion energy, $\Delta_c U$, of the complex was measured by an RBC-II rotating-bomb calorimeter

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at 298.15 K. Its standard enthalpy of combustion, $\Delta_c H_m^\theta$, and standard enthalpy of formation, $\Delta_f H_m^\theta$, were calculated.

Experimental

Chemicals

GdCl₃·4.63H₂O was prepared according to [9], sodium diethyldithiocarbamate hydrate (abbreviated as NaEt₂dtc·3H₂O, mass fraction higher than 0.995) and 1,10-phenanthroline (abbreviated as phen-H₂O, mass fraction higher than 0.995) were commercially obtained from Shanghai Regent Factory. They were maintained in desiccators over phosphorus pentoxide or silica gel before the calorimetric measurements. Absolute ethanol (analytical grade) from Xi'an Chemical Reagent Company was used to prepare all of the calorimetric solvents. Potassium chloride (mass fraction 0.9999) was purchased from Shanghai No. 1 Regent Factory, Shanghai, China, and dried in a vacuum oven at 500 K for 8 h prior to use.

Equipments and analyzes methods

Spectra were obtained with samples in KBr matrix for the title complex and ligands. A BEQ UZNDX – 550 series FT-IR spectrophotometer in the 4000–400 cm⁻¹ region was used. Gd³⁺ and Cl⁻¹ were determined volumetrically with EDTA by complexometric titration and gravimetrically; C, H, N and S contents were carried out by an instrument of Vario EL III CHNOS of Germany. TG-DTG tests were performed in a Perkin Elmer thermobalance and under dynamic atmosphere of high purity N₂ (mass fraction 0.99999) with flow rate of 60 cm⁻³ min⁻¹ and a heating rate of 10 K min⁻¹. ICP-OES spectroscopy was carried out using a Perkin Elmer ICP Liberty 150 instrument.

RD496-III heat conduction calorimeter

All the enthalpies of solutions and reaction were measured by an RD496-III microcalorimeter [10]. The heat conduction microcalorimeter is mainly composed of the precision temperature controlling system, the electric energy calibration system, the thermostat and the data processing system. The working temperature of the calorimeter lies in the range of 77.15–473.15 K. It equips a 16 mL sample cell and 16 mL reference cell. The thermal effect can be determined through a thermoelectric pile composed of 496 thermocouples, which is converted to thermal electric potential. The thermal electric potential is amplified through a microvolt amplifier, converted by modulus, collected and processed by a computer. The functions of control-

ling the temperature of the system, running on chemical and electrical calibrations, having the sensitivity calibrated, measuring the thermal effect, and picking up and saving the results are achieved by a program under a Window system designed by ourselves.

The baseline stability was determined at a constant temperature and with a rising temperature at a stated heating rate. Keeping the temperature at 313.15 K for 50 h, the baseline change was less than ±0.2 μV. While raising the temperature from 313.15 to 373.15 K at the speed of 1 K h⁻¹, the stability is 0.4 μV K⁻¹.

The reliability of the calorimeter was verified by measuring the dissolution enthalpy of KCl (calorimetrically primary standard) in double distilled water at 298.15 K. According to molar ratio of KCl to water, $n_{\text{KCl}} : n_{\text{H}_2\text{O}} \approx 1:500$, certain amount of KCl is dissolved in double distilled water at $T = (298.15 \pm 0.001)$ K. The average enthalpy of dissolution of KCl determined from the 6 tests was, $\Delta_s H_{m,\text{KCl}}^\theta = (17.238 \pm 0.048)$ J mol⁻¹, as shown in Table 1, which is in agreement with the published value (17.536 ± 3.4) J mol⁻¹ [11]. Compared with the recommended reference data, the inaccuracy and the uncertainty of the experimental results were within 0.02 and 0.3%, respectively.

Table 1 Enthalpy of solution of KCl in deionized water at 298.15 K

No. of experiments	<i>m/g</i>	<i>r</i>	$\Delta_{\text{sol}} H_m^\theta / \text{kJ mol}^{-1}$
1	0.0663	499	17.602
2	0.0667	496	17.646
3	0.0670	494	17.677
4	0.0660	502	17.475
5	0.0664	499	17.474
6	0.0661	501	17.612
mean			17.581 ± 0.039
literature [11]			17.584 ± 0.007

RBC-II rotating-bomb combustion calorimeter

The constant-volume combustion energy of the compound was measured by an RBC-type II precision rotating bomb combustion calorimeter [12]. It mainly consisted of a thermostatic through with an outer casing, a calorimetric tube and a system for the temperature measurement. The volume of the thermostatic through was about 25.0 dm³ and equipped with two interior agitators. The temperature of the thermostatic water in the bath was automatically maintained at $T = (298.15 \pm 0.001)$ K by means of a precise thermosistor. The volume of the calorimetric tube was 4.5 dm³. The temperature gauge from the digital indicator with integrated circuit was used to measure the temperature of the calorimetric tube. The bicyclic structure of the crucible support in the oxygen bomb was constructed so that the bomb can

make a compound rotation about an axis perpendicular to the bomb axis (i.e., end-over-end rotation) and about the bomb axis (axial rotation) at the same time.

The thermostatic water bath of the outer casing was controlled at $T=(298.15\pm 0.001)$ K, then the water temperature in the calorimetric tube was adjusted to a temperature lower than that of the water bath of the outer casing, and it was assured that the range of the temperature change in the calorimetric tube was half of the total temperature rise of the calorimeter after the combustion was completed. When adding a known amount of pure water to the calorimetric tube, laying the sample into the crucible fixed onto the support in the rotating bomb but not fallen into the solution, fastening the combustion fuse in the support pillars of the bomb, injecting the initial bomb solution into the rotating bomb, and filling the bomb with 2.533 MPa of oxygen have been completed, subsequently the bomb was sealed. Besides, it was important for the temperature change of the calorimeter to keep constant at the beginning of every experiment. In the initial stage of the experiment, the temperature reading was recorded every 30 s until the tenth one has been recorded. From the eleventh reading, the sample was ignited and the temperature reading was recorded one time per minute till the rate of the temperature change kept invariable. It was assumed that the main period (15 min) of the combustion reaction was finished at this stage. During the final state of the experiment, the temperature reading was made every 30 s and recorded for 10 times.

The temperature rise must be corrected on the basis of the heat exchange between the calorimetric tube and its surroundings. The correction value of the heat exchange was calculated by means of the following equation according to the literature [13]:

$$\zeta = \left(\frac{V_n - V_0}{\theta_n - \theta_0} \right) \left(\frac{T_0 + T_n}{2} + \sum_{i=1}^{n-1} T_i - n\theta_n \right) + nV_n \quad (1)$$

where ζ (K) denotes the correction value of the heat exchange; n , the number of readings for the main (or reaction) stage; V_n and V_0 (K min⁻¹), the temperature drift rates in the final and initial stages, respectively (V is positive when the temperature decreases); θ_n and θ_0 (K), the average temperatures of the calorimeter during the final and initial stages, respectively; T_0 (K), the last reading of the initial stage; T_n (K), the first reading of the final stage; $\sum_{i=1}^{n-1} T_i$, the sum of all the temperature readings, except for the last one, of the main stage; $(V_n - V_0)/(\theta_n - \theta_0)$, a constant relative to the calorimeter performance.

After the experiment ended, the final products of the combustion reaction were analyzed [12]. The gases

formed in the combustion were collected in a gas-collecting bag. It was measured by a gas meter which was fitted between the bag and the bomb. The gaseous carbon dioxide produced in the combustion was absorbed by a weighed absorption tube containing alkali asbestos. The amount of CO₂(g) was determined through the mass increment of the tube after absorbing the carbon dioxide. The amount of CO₂(g) dissolved in the final solution was neglected. Four absorption tubes were connected in series with each other for the measurement. The first was filled with P₄O₁₀ and CaCl₂ (anhydrous) to absorb the water vapor contained in the gas, the second was filled with active MnO₂ in order to absorb the nitrogen oxides, the third was filled with alkali asbestos to absorb the CO₂, and the fourth was full of the solid P₄O₁₀ and CaCl₂ (anhydrous) to absorb the water formed in the determination. The nitrogen oxides (NO_x) produced from oxidation of a trace of nitrogen contained in the bomb mainly existed in the form of the NO₂ due to the excess of oxygen in the bomb, as shown by the results obtained according to the procedure in the literature [12], and no NO₂ appeared in the gas phase because it was readily dissolved in the water poured into the bottom of the bomb to form the aqueous nitric acid.

The fittings and the inside wall of the bomb were washed for three times using distilled water at first, then the bomb solution including the washing solution was completely transferred to a conical bottle and heated to boiling to remove a little amount of CO₂ dissolved in the bomb solution. The total amount of nitric acid was obtained from titrating the solution to a phenolphthalein end-point with a standard solution of NaOH. Since the crucible in the rotating bomb was attached to the support, the final solid products were left in the crucible at the end of the experiment. The results of the IR spectra, chemical and elementary analyses have been shown that the final solid product was only metal oxide. The analyzes of the combustion products indicated that the compound was combusted to the CO₂(g), H₂O(l) and Gd₂O₃(s) under the excessive oxygen. The amount of NO_x and CO in the final gas phase may be neglected.

The energy equivalent of the RBC-type II calorimeter was determined from 6 combustion experiments using about 0.8 g of NIST 39i benzoic acid with a certified massic energy of combustion $\Delta_c U = -(26434 \pm 3)$ J g⁻¹ under the same experimental conditions to be: $\epsilon_{\text{calor}} = (17775.09 \pm 7.43)$ J K⁻¹ by the formula (2). The calibrated experimental results with an uncertainty $4.68 \cdot 10^{-4}$ are summarized in Table 2.

$$\epsilon_{\text{calor}} = \frac{\Delta_c U a + G b + 59.8 V N}{\Delta T} \quad (2)$$

Table 2 Result for calibration of energy equivalent of the rotating-bomb calorimeter

No.	Mass of complex, <i>m</i> /g	Calibrated heat of combustion wire, <i>q_c</i> /J	Calibrated heat of acid, <i>q_N</i> /J	Calibrated, ΔT /K	Energy equivalent, <i>W</i> /J K ⁻¹
1	0.99702	10.35	24.78	1.4834	17790.45
2	0.78940	8.10	20.89	1.1746	17789.88
3	0.83060	12.60	20.43	1.2382	17758.93
4	0.96869	12.60	17.43	1.4418	17780.82
5	0.99485	12.60	20.80	1.4800	17798.18
6	1.12328	9.09	21.85	1.6735	17761.41
7	0.90036	9.28	21.67	1.3429	17745.97
mean					17775.09±7.43

where ϵ_{calor} (J K⁻¹) was the energy equivalent of the calorimeter; $\Delta_c U$ (J g⁻¹), the massic energy of combustion of benzoic acid; *a*/g, the mass of a pellet of benzoic acid; *G* (J cm⁻¹), the combustion enthalpy of Ni–Cr wire for ignition ($G=0.9$ J cm⁻¹); *b* (cm), the length of the actual Ni–Cr wire consumed in ignition; 59.8 kJ mol⁻¹, the energy of formation of aqueous nitric acid, based on the molar energy of formation of HNO₃(aq) from N₂(g), O₂(g) and H₂O(l), $\Delta_f H_m^0=59.8$ kJ mol⁻¹ [12, 13], for 0.1 mol dm⁻³ of HNO₃(aq); *V* (cm³), the volume of the consumed sodium hydroxide solution; *N* (mol dm⁻³), the molar concentration of the sodium hydroxide solution used in the neutral titration of the nitric acid, often $N=0.1000$ mol dm⁻³; ΔT , the corrected temperature rise of the combustion or reaction, $\Delta T=(T_n-T_0)+\zeta$, as obtained from the Eq. (1).

Synthesis of the complex

GdCl₃·4.63H₂O, one equivalent of phen·H₂O and three equivalents of NaEt₂dtc were dissolved in a minimal amount of absolute ethanol, respectively. To the mixed ethanolic solution of phen·H₂O and NaEt₂dtc, the ethanolic solution of salt was slowly drop-wise under electromagnetically stirring. The reaction mixture was allowed to stand for 30 min resulting in the precipitant. The solid formed was filtered and rinsed three times with small portions of absolute ethanol. The resulting crystal was dried in vacuum and stored in a desiccator over P₄O₁₀ ready to be used.

Results and discussion

Characterization of the complex

The elemental analyses results of the title complex are as follows: *m*_{found}: Gd 20.12%, C 41.44%, H 4.91%, N 8.97%, S 24.56%; *m*_{calculated}: Gd 20.10%, C 41.46%, H 4.90%, N 8.95%, S 24.59%, which is identified as the formula of Gd (Et₂dtc)₃(C₁₂H₈N₂). TG-DTG tests

reveal the complex possesses quite thermal stability and the decomposition temperature is above 485 K.

The preliminary identification regarding the nature of bonding of the ligands phen·H₂O and NaEt₂dtc has been obtained from the bonds obtained in the IR spectra, as depicted in Fig. 1. The IR spectra reveal that both phen·H₂O and NaEt₂dtc moieties have been coordinated to the metal ion [14, 15]. Compared with the spectra of salt, NaEt₂dtc·3H₂O and phen·H₂O (3390, 3366, 3388 cm⁻¹), the characteristic absorption of hydroxyl group in water is not present in the complex. Compared to those of the ligand phen, the peaks of 1624, 1589, 1572 and 1516 cm⁻¹ are assigned as skeleton vibration of benzene ring and the bands of 854 and 739 cm⁻¹ are assigned to the bend vibration of C–H in the complex. These vibrations are found to be positively shifted suggesting the coordination of two nitrogen atoms of phen

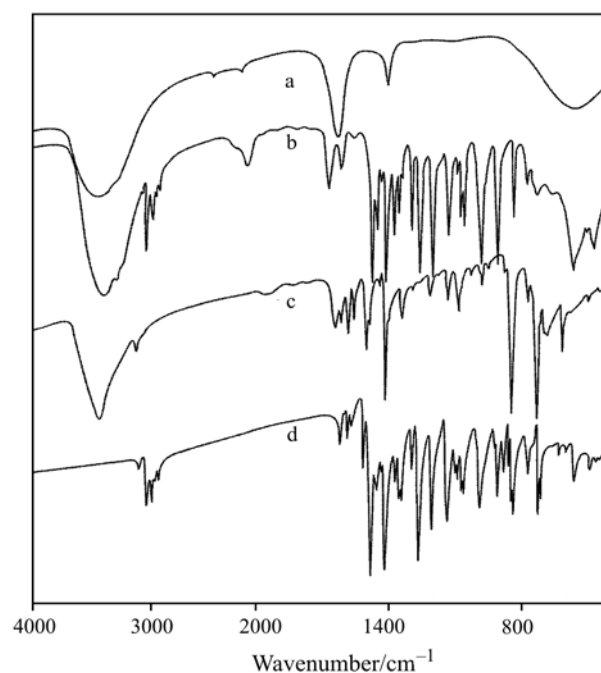
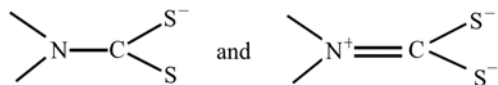
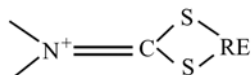


Fig. 1 Comparison of IR spectra of a – GdCl₃·4.63H₂O, b – NaEt₂dtc·3H₂O, c – phen·H₂O and d – complex

to Eu³⁺. In contrast with that of 1477 cm⁻¹ in the ligand NaEt₂dtc·3H₂O, ν_{CN} shifts to higher wave number of 1510 cm⁻¹, and presents a double-bond character in the complex, which can be attributed to that NCS₂⁻ group has two main forms of vibration [16]:



The vibration intensity of the later is enhanced when the two sulfur atoms of ligand coordinate to Gd³⁺ to form a tetra-atomic ring

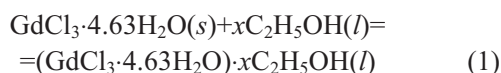


accordingly ν_{CN} moves to the higher wave number. And an increase of 11 cm⁻¹ of ν_{CSS} stretching band is observed compared to that of ligand as well. Obviously, the resulting tetra-atomic ring increases the vibration intensity of ν_{CN} [15]. The changes of ν_{CN} and ν_{CSS} indicate that the two sulfur atoms of ligand coordinate to Gd³⁺ in a bidentate manner.

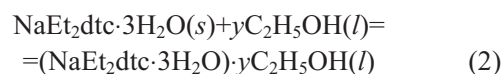
Calculation of the standard molar enthalpy change of the title solid-phase reaction

The enthalpies of dissolution of GdCl₃·nH₂O and ligand were obtained at 298.15 K as previously reported [8]. The calorimetric experiments in details were performed in following procedures.

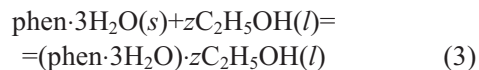
Sample of 0.32 mmol GdCl₃·4.63H₂O(s) was dissolved in 8 dm³ absolute ethanol at 298.15 K, as shown in reaction (1).



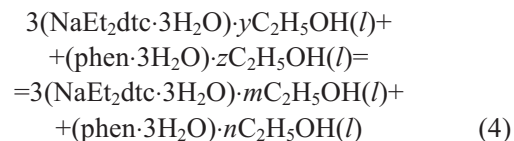
Sample of 0.16 mmol [NaEt₂dtc·3H₂O(s)] was dissolved in 8 dm³ absolute ethanol at 298.15 K, as presented in reaction (2).



Sample of 0.16 mmol phen·3H₂O(s) was dissolved in 8 dm³ absolute ethanol at 298.15 K, which is represented in reaction (3).

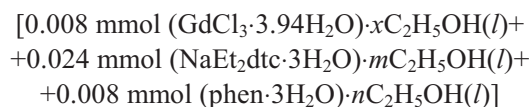


Sample of ethanolic solution 0.024 mmol 3(NaEt₂dtc·3H₂O)·yC₂H₅OH(l) and that of 0.008 mmol (phen·3H₂O)·zC₂H₅OH(l) were mixed with the stoichiometric ratio at 298.15 K, which is represented in reaction (4).

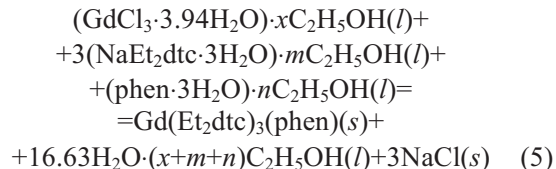


where y+z=m+n.

Samples of ethanolic solutions:



were mixed at 298.15 K, which is reflected in reaction (5).



The enthalpies of solution, Δ_{sol}H_m⁰(1), Δ_{sol}H_m⁰(2) and Δ_{sol}H_m⁰(3) of GdCl₃·4.63H₂O, NaEt₂dtc·3H₂O and phen·H₂O in absolute ethanol are given in Table 3, respectively, while they dissolve as alcoholate compound in absolute ethanol. The mixed enthalpy of the ethanolic solution of two ligands Δ_{mix}H_m⁰ and the enthalpy change of the liquid-phase reaction Δ_rH_m⁰(l) are listed in Table 4.

The application of Hess' law to the series of reactions (1)–(5) and the title solid-reaction (6) gives

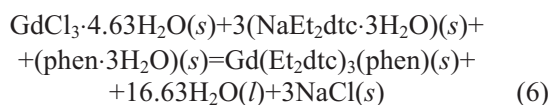
Table 3 Experimental data of Δ_{sol}H_m⁰(1), Δ_{sol}H_m⁰(2) and Δ_{sol}H_m⁰(3)

No.	m/mg	Q/mJ	Δ _{sol} H _m ⁰ (1)/ kJ mol ⁻¹	m/mg	Q/mJ	Δ _{sol} H _m ⁰ (2)/ kJ mol ⁻¹	m/mg	Q/mJ	Δ _{sol} H _m ⁰ (3)/ kJ mol ⁻¹
1	83.32	-5374.383	-22.384	36.07	7935.321	49.566	31.71	3351.540	20.950
2	83.32	-5283.494	-22.005	36.02	7916.679	49.518	31.77	3393.602	21.173
3	83.28	-5318.801	-22.162	36.09	8010.432	50.007	31.76	3343.271	20.866
4	83.28	-5415.149	-22.564	36.02	7911.509	49.485	31.73	3356.008	20.965
5	83.30	-5326.451	-22.189	36.05	7968.605	49.801	31.68	3315.208	20.746
6	83.30	-5398.974	-22.491	36.04	7972.883	49.842	31.73	3379.615	21.123
mean			-22.299±0.096			49.703±0.094			20.970±0.071

Table 4 Experimental data of $\Delta_{\text{mix}}H_{\text{m}}^{\ominus}$ and $\Delta_{\text{r}}H_{\text{m}}^{\ominus}(1)$

No.	Q_1/mJ	$\Delta_{\text{mix}}H_{\text{m}}^{\ominus}/\text{kJ mol}^{-1}$	Q_2/mJ	$\Delta_{\text{r}}H_{\text{m}}^{\ominus}/\text{kJ mol}^{-1}$
1	73.360	9.170	-93.378	-11.672
2	74.266	9.283	-92.762	-11.595
3	72.746	9.093	-92.998	-11.624
4	73.096	9.137	-93.155	-11.644
5	74.097	9.262	-93.395	-11.674
6	71.842	8.980	-92.457	-11.557
mean	72.234±0.401	9.154±0.050	93.024±0.164	-11.628±0.0204

a thermochemical cycle, from which the enthalpy change of the reaction (6) is derived.



So, the enthalpy change of the title solid-phase reaction at 298.15 K can be calculated as (140.354±0.483) kJ mol⁻¹ according to Eq. (7).

$$\begin{aligned} \Delta_{\text{r}}H_{\text{m}}^{\ominus}(s) &= \Delta_{\text{sol}}H_{\text{m}}^{\ominus}(1) + 3\Delta_{\text{sol}}H_{\text{m}}^{\ominus}(2) + \\ &+ \Delta_{\text{sol}}H_{\text{m}}^{\ominus}(3) + \Delta_{\text{mix}}H_{\text{m}}^{\ominus} + \Delta_{\text{r}}H_{\text{m}}^{\ominus}(l) = \\ &= [(-22.299 \pm 0.096) + 3(49.703 \pm 0.094) + \\ &+ (20.970 \pm 0.071) + (9.154 \pm 0.050) + \\ &+ (-11.628 \pm 0.0204)] \text{ kJ mol}^{-1} = \\ &= (145.306 \pm 0.519) \text{ kJ mol}^{-1} \end{aligned} \quad (7)$$

Calculation of the thermodynamic parameters of liquid-phase reaction

The final product from liquid-phase reaction was collected, purified and characterized by IR and ICP as the same with the as-prepared one, showing that the liquid-phase reaction (4) is irreversible. The calorimetric experiment illustrates that the reaction is exo-

thermic. Based on thermokinetic data of liquid-phase reaction at different temperatures shown in Table 5, and on the thermodynamic equations [17], the thermodynamic parameters and kinetic parameters of the liquid reaction are obtained and shown in Table 6. Apparently, the liquid-phase reaction is of the first order. The apparent Gibbs free energy increases with increasing the temperature, reflecting that the liquid-phase reaction readily occurs in the temperature range from 292.15 to 301.15 K.

Results of combustion energy

Combustion energy of the complex

The determination method of combustion energy for the complex was the same as for the calibration of the calorimeter with benzoic acid. The combustion energies of the samples were calculated by the Eq. (2). The results of the calculations are given in Table 7.

Standard combustion enthalpy of complex

The standard combustion enthalpy of the complex, $\Delta_{\text{c}}H_{\text{m}}^{\ominus}$ (complex, s, 298.15 K), refers to the combus-

Table 5 Thermokinetic data of liquid-phase of formation reaction

Time/s	292.15 K		Time/s	295.15 K		Time/s	298.15 K		Time/s	301.15 K	
	H_i/H_0	dH_i/dt		H_i/H_0	dH_i/dt		H_i/H_0	dH_i/dt		H_i/H_0	dH_i/dt
160	0.4282	4.8201	150	0.3819	4.2477	170	0.6363	2.6604	165	0.7723	1.5625
165	0.4418	4.7573	155	0.3969	4.1850	175	0.6528	2.5821	170	0.7902	1.5000
170	0.4553	4.6945	160	0.4118	4.1380	180	0.6689	2.5195	175	0.8074	1.4219
175	0.4686	4.6160	165	0.4264	4.0753	185	0.6845	2.4413	180	0.8238	1.3438
180	0.4817	4.5689	170	0.4408	3.9969	190	0.6998	2.3630	185	0.8394	1.2656
185	0.4946	4.4747	175	0.4550	3.9342	195	0.7145	2.3004	190	0.8542	1.2031
190	0.5073	4.4119	180	0.4690	3.8872	200	0.7289	2.2378	195	0.8682	1.1250
195	0.5198	4.3491	185	0.4827	3.8245	205	0.7428	2.1596	200	0.8813	1.0625
200	0.5321	4.2706	190	0.4962	3.7618	210	0.7562	2.0813	205	0.8936	9.8438
205	0.5442	4.2078	195	0.5095	3.6991	215	0.7692	2.0187	210	0.9052	9.2188
210	0.5561	4.1450	200	0.5225	3.6364	220	0.7818	1.9562	215	0.9159	8.5938

$$H_0 = 0.194221 \text{ J (292.15 K)}, 0.133016 \text{ J (295.15 K)}, 0.092998 \text{ J (298.15 K)} \text{ and } 0.060929 \text{ J (301.15 K)}$$

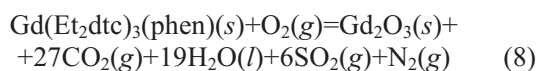
Table 6 Kinetic, thermodynamic parameters of liquid-phase reaction

Temperature/K	$k \cdot 10^3/s^{-1}$	n	r^a	$E/kJ mol^{-1}$	$\ln A/s^{-1}$	r^a	$\Delta G_{\neq}^{\theta}/kJ mol^{-1}$	$\Delta H_{\neq}^{\theta}/kJ mol^{-1}$	$\Delta S_{\neq}^{\theta}/J mol^{-1} K^{-1}$	r^a
292.15	3.4857	0.605	0.999				85.25			
295.15	4.2727	0.603	0.999				85.65			
298.15	5.2722	0.604	0.999	48.74	14.410	0.999	86.02	46.28	-133.373	0.999
301.15	6.3272	0.607	0.999				86.46			

^a r – the linear correlation coefficient**Table 7** Combustion energy of Gd(Et₂dtc)₃(phen)

Sample	No.	Mass of sample, m/g	Calibrated heat of combustion wire, Q_c/J	Calibrated heat of acid, Q_N/J	Calibrated, $\Delta T/K$	Combustion energy of sample, $-\Delta_c U/J g^{-1}$
Gd(Et ₂ dtc) ₃ (phen)	1	0.80140	12.60	1633.22	1.1686	23865.92
	2	0.81258	12.60	1656.00	1.1857	23883.59
	3	0.80035	12.60	1631.08	1.1664	23851.05
	4	0.79857	12.60	1627.45	1.1666	23913.21
	5	0.80820	12.60	1647.07	1.1787	23870.12
	6	0.81357	12.60	1658.02	1.1852	23814.12
	mean					23870.84±10.42

tion enthalpy change of the following ideal combustion reaction at 298.15 K and 100 kPa.



The standard combustion enthalpy of the complex calculated by the Eqs (9) and (10)

$$\Delta_c H_m^{\theta}(\text{complex}(s) \text{ 298.15 K}) = \Delta_c U(\text{complex}(s) \text{ 298.15 K}) + RT \quad (9)$$

$$\Delta n = n_g(\text{products}) - n_g(\text{reactants}) \quad (10)$$

where n_g is the total amount in mole of gases present as products or as reactants, $R=8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $T=298.15 \text{ K}$. The result of the calculation was $(-18692.92 \pm 8.15) \text{ kJ mol}^{-1}$.

Standard enthalpy of formation of the complex

The standard enthalpy of formation of the complex, $\Delta_f H_m^{\theta}(\text{complex}(s) \text{ 298.15 K})$, are calculated by Hess' law according to the Eq. (2).

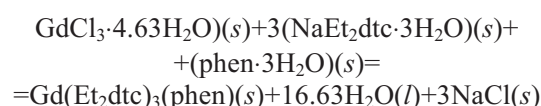
$$\begin{aligned} \Delta_f H_m^{\theta} \text{Gd}(\text{Et}_2\text{dtc})_3(\text{phen})(s) = & \\ = [0.5\Delta_f H_m^{\theta} \text{Gd}_2\text{O}_3(s) + 27\Delta_f H_m^{\theta} \text{CO}_2(g) + & \\ + 19\Delta_f H_m^{\theta} \text{H}_2\text{O}(l) + & \\ + 6\Delta_f H_m^{\theta} \text{SO}_2(g) + 2.5\Delta_f H_m^{\theta} \text{N}_2(g)] - & \\ - \Delta_c H_m^{\theta} \text{Gd}(\text{Et}_2\text{dtc})_3(\text{phen})(s) & \quad (11) \end{aligned}$$

where $\Delta_f H_m^{\theta} \text{Gd}_2\text{O}_3(s) = (-1815.60 \pm 3.60) \text{ kJ mol}^{-1}$,
 $\Delta_f H_m^{\theta} \text{CO}_2(g) = (-393.51 \pm 0.13) \text{ kJ mol}^{-1}$,
 $\Delta_f H_m^{\theta} (\text{H}_2\text{O}(l)) = (-285.830 \pm 0.042) \text{ kJ mol}^{-1}$,

$\Delta_f H_m^{\theta} (\text{SO}_2(g)) = (-296.81 \pm 0.20) \text{ kJ mol}^{-1}$ [18]. Solving the Eq. (11), the standard enthalpy of formation of Gd(Et₂dtc)₃(phen)(s) is calculated as $(-51.28 \pm 9.17) \text{ kJ mol}^{-1}$.

Conclusions

Using a precise heat conduction calorimeter through a designed thermochemical cycle, the standard molar enthalpy of reaction for the title solid-phase reaction:



were derived as $(145.306 \pm 0.519) \text{ kJ mol}^{-1}$ at 298.15 K. Based on thermokinetic data of liquid-phase reaction at different temperatures, the thermodynamic parameters and kinetic parameters of the liquid reaction are obtained. From the combustion energy of the complex determined by an RBC-II rotating-bomb calorimeter and other auxiliary thermodynamic qualities, the standard enthalpy of formation of Gd(Et₂dtc)₃(phen)(s) have been deduced to be: $(-51.28 \pm 9.17) \text{ kJ mol}^{-1}$.

Acknowledgements

The Authors thank the financial support from the National Natural Science Foundation of China (Grant No. 20171036), Education committee of Shannxi Province (Grant Nos 01JK229 and FF02328).

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Received: July 12, 2004

In revised form: March 21, 2005

DOI: 10.1007/s10973-005-6518-x