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SOLUTION THERMOCHEMISTRY OF DIETHYLDITHIOCARBAMATO–IRON(III)

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ABSTRACT

The enthalpy change (303 K) for the standard state solid phase complexation reaction

$$FeCl_3(c) + 3NaS_2CN(C_2H_5)_2(c) \xrightarrow{\Delta H_R^\circ} Fe[S_2CN(C_2H_5)_2]_3(c) + 3NaCl(c)$$

is derived using conventional solution calorimetric techniques ($\Delta H_R^\circ = -82.7 \pm 2.0$ kJ mol^{-1}). Knowledge of ΔH_R° is a necessary pre-requisite for the future derivation of the Fe–S thermochemical bond energy.

INTRODUCTION

Thermochemical data for metal derivatives of dialkyldithiocarbamic acids are sparse. D'Ascenzo and Wendlandt[1] have reported TGA/DTA data for cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), mercury(II), silver(I), iron(II) and iron(III)[2] diethyldithiocarbamates, and D'Ascenzo et al.[3], have given the detailed TGA behaviour of tin(IV) diethyldithiocarbamate. Bernard and Borel[4] have also presented detailed thermoanalytical data for zinc(II), cadmium(II) and lead(II) dithiocarbamates. However, no calorimetric data exist for the metal dialkyldithiocarbamates.

This paper reports the enthalpy change (303 K) for the standard state reaction:

$$FeCl_3(c) + 3NaS_2CN(C_2H_5)_2(c) \rightarrow Fe[S_2CN(C_2H_5)_2]_3(c) + 3NaCl(c).$$

It is not possible to report the standard heat of formation of diethyldithiocarbamato–iron(III), as the necessary thermal data relating to the diethyldithiocarbamate ligand itself are not available.

EXPERIMENTAL

Calorimeter

The calorimeter used was the Tronac, Model 450 solution calorimeter (non-isothermal constant temperature environment type). The thermostat bath was maintained at 303±0.001 K, using the Tronac Model 1040 temperature controller. The reaction vessel used was a 40 cm^3 rapid response dewar. The corrected temperature changes ΔT (reaction) and $\Delta\theta$ (calibration) were derived directly from an analysis of the charted thermograms using the Dickinson extrapolation technique[5].

The calorimeter was 'tested' using the THAM reaction[6]. 'THAM' sample: NBS Standard Reference Material No. 724, dried by the recommended procedure[7].

Sample preparation

Ferric diethyldithiocarbamate was prepared by adding an aqueous solution of sodium diethyldithiocarbamate slightly in excess of the stoichiometric value to an aqueous solution of $FeCl_3 \cdot 6H_2O$. The resultant precipitate was filtered and washed thoroughly with distilled water. The complex was recrystallised in chloroform repeatedly until well-formed black crystals were obtained. The crystals were filtered off, washed with chloroform and dried in a vacuum desiccator (m.p. = 248–253 °C; literature value = 252–255 °C)[8].

Microanalysis of $Fe[(C_2H_5)_2NCS_2]_3$:

%	*C*	*H*	*N*	*S*
Calculated	35.98	6.04	8.40	38.42
Found	35.85	5.91	7.86	38.70

Sodium diethyldithiocarbamate (May and Baker) and sodium chloride (Analar) were used without further purification.

Dioxan (May and Baker) was purified according to the method outlined by Vogel[9].

Anhydrous ferric chloride

The BDH analar grade material was used without further purification. The process of weighing, filling and sealing of ampoules was performed rapidly under nitrogen to minimise decomposition of the compound.

Ferric chloride hexahydrate

The BDH analar grade material was used without further purification.

RESULTS AND DISCUSSION

Coucouvanis[10] reported that diethyldithiocarbamato–iron(III) is completely decomposed in hydrochloric acid yielding carbon disulphide and the diethylamine salt. An attempt was made to reproduce this reaction in the calorimeter with the aim of deriving the standard enthalpy of decomposition of the complex. However, it was

TABLE I

'THAM' TEST REACTION

Heat of reaction of 'THAM' (Tris(hydroxymethyl)aminomethane) with excess 0.1M HCl; 303 K. ε = total heat capacity of calorimetric system; $\Delta\theta$ = corrected temperature change (electrical calibration); t = heating period (electrical calibration); R_s = calibration standard resistance; HTR V = potential drop across calorimeter heater; HTR I = potential drop across R_s; ΔT = corrected temperature change (reaction); $\varepsilon = (\text{HTR V})(\text{HTR I})t/(R_s\Delta\theta)$ A sec; $\Delta H = \varepsilon\Delta T/n$ kJ mol^{-1}.

Run No.	*THAM mass (g)*	*Moles THAM* $\times 10^{-4}$	ε ($\times 10^3$) *(A sec)*	ΔT *(mV)*	$-\Delta H^\circ_{\text{THAM}}$[a] *(kJ mol^{-1})*
I	0.04369	3.6066	10.5786	0.9920	29.097
II	0.11663	9.6277	10.8203	2.5694	28.840

Calibration No.	t *(sec)*	*HTR V (V)*	*HTR I (V)*	$\Delta\theta$ *(mV)*	$R_s(\Omega)$	ε ($\times 10^3$) *(A sec)*
I	60	6.4139	6.1128	2.2222	100.07	10.5786
II	60	6.4150	6.1119	2.1726	100.07	10.8203

[a] Average $\Delta H^\circ_{\text{THAM}} = -28.97 \pm 0.13$ kJ mol^{-1} (literature[6] $\Delta H_{\text{THAM}} = -28.89 \pm 0.01$ kJ mol^{-1}). The working performance of the calorimeter is thus shown to be satisfactory.

found that dilute and concentrated hydrochloric acid failed to dissolve or decompose the complex at 303 K, and hence this reaction was abandoned as a potential standard state thermochemical reaction for deriving the standard heat of formation of diethyldithiocarbamato–iron(III) at ambient temperatures.

The standard enthalpy change for the following solid phase standard state reaction was derived

$$\text{FeCl}_3(\text{c}) + 3\text{Na}(\text{S}_2\text{CNEt}_2)(\text{c}) \rightarrow \text{Fe}(\text{S}_2\text{CNEt}_2)_3(\text{c}) + 3\text{NaCl}(\text{c})$$

(303 K), by measuring sequentially the heat of solution of ferric chloride (or ferric chloride hexahydrate) and sodium diethyldithiocarbamate in a dioxan–water–acetone solvent (volume ratio 3:1:1), followed by the sequential measurement of the heat of

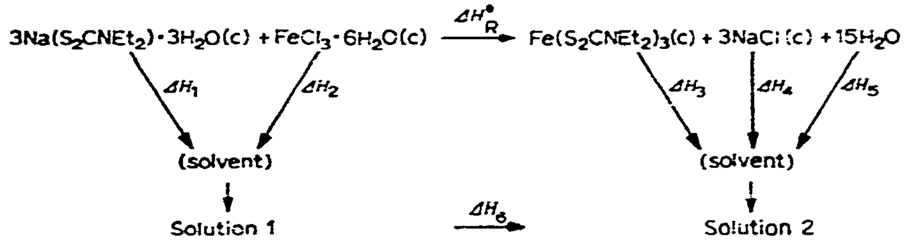

Fig. 1. Scheme for deriving standard state heat of reaction ΔH°_R. ΔH_1 represents the heat of solution of $\text{Na(S}_2\text{CNEt}_2)\cdot 3\text{H}_2\text{O}$; ΔH_2 is the heat solution of $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ plus the heat of reaction in solution between $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ and $\text{Na(S}_2\text{CNEt}_2)\cdot 3\text{H}_2\text{O}$.

solution of diethyldithiocarbamato–iron(III) and sodium chloride in a second batch of the same solvent. Preliminary tests indicated that complete solubility of all components was effected at 303 K. The relevant thermochemical cycle is given in Fig. 1.

From the first law of thermodynamics the following equation is obtained:

$$3\Delta H_1 + \Delta H_2 + \Delta H_6 - \Delta H_3 - 3\Delta H_4 - 15\Delta H_5 - \Delta H_R^\circ = 0$$

As strict stoichiometric qualities of reactants and products were taken, Solution 1 has the same chemical identity as Solution 2. This was verified by their identical UV

TABLE 2

HEAT CAPACITY DATA (303 K)

No.[a]	*t (sec)*	*HTR V (V)*	*HTR I (V)*	$\Delta\theta$ *(mV)*	$R_s(\Omega)$	ε *(× 10^3) (A sec)*
1	120	6.4114	6.1129	6.9841	100.07	6.7293
2	120	2.9224	2.7809	5.5924	100.07	1.6372
3	90	1.4661	1.3945	0.2381	100.07	7.7226
4	120	0.1430	0.9181	0.1429	100.07	1.1011
5	120	6.4124	6.1125	7.1429	100.07	6.5802
6	60	6.4131	6.1126	3.5714	100.07	6.5812
7	60	8.9939	8.5931	7.0238	100.07	6.5974
8	60	8.9954	8.5928	7.1428	100.07	6.4883
9	60	6.4145	6.1134	3.5913	100.07	6.5470
10	60	6.4143	6.1133	3.5804	100.07	6.5666

[a] The identification numbers refer to the following calorimetric experiments. 1, 8 = the addition of sodium diethyldithiocarbamate to the solvent; 2, 6 = the addition of anhydrous ferric chloride to sodium diethyldithiocarbamate solution; 9, 10 = the addition of hydrated ferric chloride to sodium diethyldithiocarbamate solution; 5, 7 = the addition of ferric diethyldithiocarbamate to the solvent; 3, 4 = the addition of sodium chloride to ferric diethyldithiocarbamate solution.

TABLE 3

REACTION ENTHALPY DATA (303 K)

No.[a]	*Mass (g)*	*No. of moles × 10^{-4}*	ε *(× 10^3) (A sec) Table 2*	ΔT *(mV)*	$-\Delta H$ *(kJ mol^{-1})*	
1	0.05438	2.4136	6.7293	14.13	393.9	ΔH_1
2	0.01252	0.7719	1.6372	19.68	417.4	ΔH_2
3	0.02913	4.9846	7.7226	0.38	5.9	ΔH_4
4	0.01961	3.3556	1.1011	0.19	6.1	ΔH_4
5	0.04845	0.9678	6.6176	22.06	1508.6	ΔH_3
6	0.01528	0.9420	6.5812	5.99	418.6	ΔH_2
7	0.05016	1.0019	6.5974	22.70	1494.7	ΔH_3
8	0.07242	3.2142	6.4883	19.60	395.7	ΔH_1
9	0.03025	1.1191	6.5470	5.40	315.7	ΔH_2
10	0.03065	1.1392	6.5666	5.42	312.5	ΔH_2

[a] See footnote to Table 2.

spectra. Hence $\Delta H_6 = 0$. ΔH_5 involves the dilution of Solution 2 with a small quantity of water. The amount of heat associated, though finite, is very small (0.01 J) compared with the other heat changes and in this work ΔH_5 is assumed negligible. ΔH_1, ΔH_2, ΔH_3 and ΔH_4 were measured and the standard state heat of reaction, ΔH_R°, was obtained from the equation:

$$\Delta H_R^\circ = 3\Delta H_1 + \Delta H_2 - \Delta H_3 - 3\Delta H_4$$

The various calorimetric data are collected in Tables 2 and 3.

All reactions were exothermic and the equilibration time following an ampoule fracture was less than 1 min in all cases; consequently all reactions were classified as fast which minimized errors due to heat leakage[11] and enhanced the validity of the Dickinson extrapolation technique[5] to determine the 'corrected' temperature changes. The mean enthalpy data (303 K) are collected in Table 4.

TABLE 4

SOLUTION THERMOCHEMICAL DATA SUMMARY FOR DIETHYLDITHIOCARBAMATO-IRON(III) SYSTEM

ΔH unit = kJ mol^{-1}.

$\Delta H_1 = -394.8 \pm 0.4$
$\Delta H_2{}^a = -314.1 \pm 0.7$
$\Delta H_2{}^b = -418.0 \pm 0.3$
$\Delta H_3 = -1501.7 \pm 0.4$
$\Delta H_4 = -6.0 \pm 0.1$
$\Delta H_R^{\circ b} = -82.7 \pm 2.0$
$\Delta H_R^{\circ a} = +21.2 \pm 2.0$

[a] Based on $FeCl_3 \cdot 6H_2O$. [b] Based on $FeCl_3$.

It is not possible to calculate the standard heat of formation of ferric diethyldithiocarbamate from ΔH_R° as the standard heat of formation of sodium diethyldithiocarbamate is unknown. The following thermochemical cycle (Fig. 2) relates ΔH_R° to ΔH_{R_g}—the enthalpy change for a gas phase reaction in which gaseous ferric diethyldithiocarbamate is formed from gaseous Fe atoms and gaseous hydrogen diethyl-

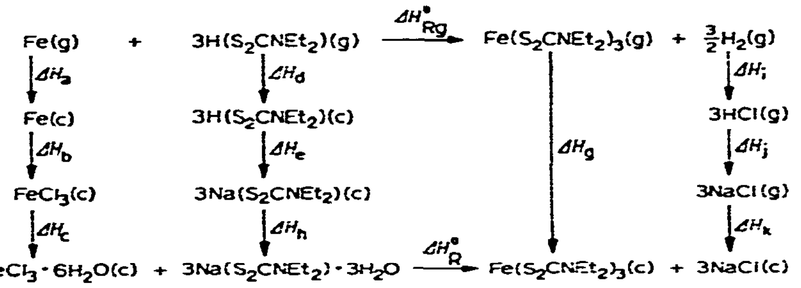

Fig. 2. Thermochemical scheme relating ΔH_R° to ΔH_{R_g}.

dithiocarbamate molecules. Derivation of ΔH_{Rg} is the first step in the calculation of the Fe–S bond energy in $\mathrm{Fe[(C_2H_5)_2NCS_2]_3}$.

Of the various enthalpy changes depicted, ΔH_d, ΔH_e, ΔH_g and ΔH_h are not available from the literature and hence at the present time it is impossible to derive $\Delta H^{\circ}_{\mathrm{Rg}}$. However, the missing data are currently being derived in this laboratory. In order to define the relative change in the standard heat of formation of diethyldithiocarbamate as a function of the coordinated metal, attempts were made to obtain $\Delta H^{\circ}_{\mathrm{R}}$ (the standard state heat of formation reaction) values for other transition metal diethyldithiocarbamates such as chromium, cobalt and manganese diethyldithiocarbamates. However, several difficulties became apparent such as insolubility of one or more components in the water–dioxan–acetone solvent and the presence of non-stoichiometric side-reactions—all making a determination of $\Delta H^{\circ}_{\mathrm{R}}$ impossible for these systems.

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REFERENCES

1 G. D'Ascenzo and W. W. Wendlandt, *J. Therm. Anal.*, 1 (1969) 423.
2 G. D'Ascenzo and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, 32 (1970) 2431.
3 G. D'Ascenzo, V. Caruchio and A. Messina, *Thermochim. Acta*, 2 (1971) 211.
4 M. A. Bernard and M. M. Borel, *Bull. Soc. Chim. Fr.*, 9 (1969) 3066.
5 S. R. Gunn, *J. Chem. Thermodyn.*, 3 (1971) 19.
6 R. J. Irving and I. Wadsö, *Acta Chem. Scand.*, 18 (1964) 195.
7 E. J. Prosen, The Standards Committee, National Bureau of Standards.
8 L. Malatesta, *Gazz. Chim. Ital.*, 69 (1939) 408.
9 A. Vogel, *Practical Organic Chemistry*, Longmans, 3rd ed., 1956, p. 177.
10 D. Coucouvanis, *Progr. Inorg. Chem.*, 11 (1970) 233.
11 I. Wadsö, *Sci. Tools*, 13 (1966) 33.