Thermochimica Acta, 33 (1979) 377—381
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Note

SOLUTION THERMOCHEMISTRY OF DIETHYLAMMONIUM DIETHYLDITHIOCARBAMATE

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(Received 14 December 1978)

Calorimetric data for metal dithiocarbamate complexes are sparse and for dialkylammonium dialkyldithiocarbamates such data are non-existent. Bernard and Borel [1] have published calorimetric data yielding standard heats of formation of bis(dithiocarbamato) Pb(II), Zn(II) and Cd(II) and Annuar et al. [2] have reported the enthalpy change at 303 K for the standard state solid phase complexation reaction

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

We have recently reported the enthalpy of sublimation of diethylammonium diethyldithiocarbamate [3] based upon vapour pressure/temperature data as derived by the Melia/Merrifield sublimation bulb technique [4]. This note reports the standard enthalpy of formation of diethylammonium diethyldithiocarbamate as derived by solution calorimetry and the heat of formation of gaseous diethylammonium diethyldithiocarbamate is calculated.

EXPERIMENTAL

Diethylammonium diethyldithiocarbamate was synthesised according to a published procedure [5] and purified by repeated sublimation. Melting point = 83—84°C; microanalysis: calculated for $C_9H_{22}N_2S_2$: C : 48.6; H : 10.0; N : 12.6; S : 28.8%; found C : 48.5; H : 9.7; N : 12.5; S : 28.6%.

Reagent grade CS_2 (May and Baker) was dried over anhydrous $CaCl_2$ and fractionally distilled. The b.p. fraction 46—47°C was collected. Diethylamine (BDH) was dried over KOH pellets and fractionally distilled. The b.p. fraction 54—55°C was collected. Dioxan was purified according to the well-established procedure [6].

The isoperibol reaction calorimeter used was the Tronac Model 450 Thermometric Titration/Reaction Calorimeter (Tronac Inc.; Orem, Utah, U.S.A.). The calorimeter was a rapid-response, glass vacuum dewar of 40 cm^3 capacity. An all-glass stirrer/ampoule beaker was employed and glass ampoules of 0.5 cm^3 capacity were used. The thermostat bath was maintained at 25.00 ± 0.001°C by employing the Tronac Model 1040 Precision Temperature Controller. Potential measurements were made using a Systron-Donner Model 7005A Digital Voltmeter and thermograms were recorded using a Perkin-

Elmer 56 multi-range strip-chart recorder. The well-defined standard procedure [7] for the measurement of enthalpy change was adopted. The calorimetric system was calibrated electrically by the standard procedure and the total heat capacity of the calorimeter and contents, ϵ, was calculated according to the equation

$$\epsilon = V_1 V_2 t (R_s \theta_c)^{-1}$$

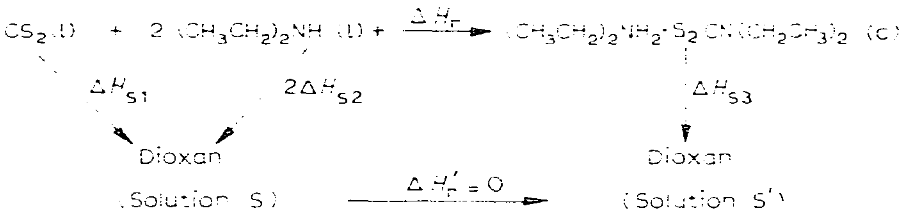
where V_1 and V_2 are the potential differences (volts) across the series standard resistance $R_s = 100.0\ \Omega$ and across the calorimeter calibration heater, respectively; t (sec) is the calibration heating period and θ_c is proportional to the corrected temperature rise during electrical calibration. For the reaction of interest $\Delta H_R = \epsilon \theta_R n_R^{-1}$ where θ_R is proportional to the corrected temperature change for the reaction as determined by Dickinson's graphical method [8] and n_R is the number of moles of the reactant defining unit reaction. The system was chemically calibrated using the thermochemical "THAM" test reaction — the measured $\Delta H^{298}_{\mathrm{THAM}} = -29.75 \pm 0.08$ kJ mole^{-1} based on five determinations: the accepted best $\Delta H^{298}_{\mathrm{THAM}} = -29.757 \pm 0.008$ kJ mole^{-1} [9]. The system was also calibrated using the dissolution of potassium chloride in water as a standard test reaction — the measured $\Delta H^{298}_{\mathrm{KCl}} = 17.55 \pm 0.12$ kJ mole^{-1} based on five determinations: the accepted best $\Delta H^{298}_{\mathrm{KCl}} = 17.548 \pm 0.012$ kJ mole^{-1} [10]. Uncertainty intervals associated with ΔH data are quoted as twice the standard deviation of the mean [11].

RESULTS AND DISCUSSION

The heterogeneous stoichiometric reaction

$$CS_2(l) + 2\,(CH_3CH_2)_2NH(l) + \rightarrow (CH_3CH_2)_2NH_2 \cdot S_2CN(CH_2CH_3)_2(c)$$

was used as the basis for calculation of the standard heat of formation of diethylammonium diethyldithiocarbamate. All three components of the reaction dissolved instantaneously at 298 K in dioxan. The relevant thermochemical cycle is given in Scheme 1.



Scheme 1

ΔH_{S1}, ΔH_{S2} and ΔH_{S3} were measured experimentally. The concentration of each component was maintained within the range 10^{-3} to 10^{-4} M and therefore all measured heats correspond to the infinite dilution values. Since strict control of stoichiometry is maintained throughout, solutions S and S' (Scheme 1) are thermodynamically equivalent and thus

$$\Delta H_r = \Delta H_{S1} + 2\Delta H_{S2} - \Delta H_{S3} \tag{1}$$

TABLE 1

Heat capacity data. Dissolution of carbon disulphide in dioxan

Calibration no.	θ_c (mV)	V_1 (volts)	V_2 (volts)	t (sec)	Heat capacity ϵ (amp sec) $\cdot 10^3$
1	0.420	2.0846	1.9732	45	4.4400
2	0.421	2.0844	1.9730	45	4.3926
3	0.448	2.0847	1.9730	45	4.1286
4	0.425	2.0847	1.9729	45	4.3518
5	0.440	2.0847	1.9729	45	4.2034
6	0.435	2.0846	1.9730	45	4.2517
7	0.443	2.0848	1.9731	45	4.1756
8	0.430	2.0848	1.9730	45	4.3016

Determination of ΔH_{S1}^{298}

Ampoules were loaded with pure liquid carbon disulphide (0.2 → 0.4 mmoles), and were broken into 40 cm^3 of dioxan in the calorimeter vessel. Data yielding ΔH_{S1}^{298} are given in Tables 1 and 2.

Determination of ΔH_{S2}^{298}

Ampoules were loaded with diethylamine (0.3—0.6 mmoles). The calorimeter was filled with a solution of carbon disulphide in dioxan (10^{-2} M). Data leading to ΔH_{S2}^{298} are recorded in Tables 3 and 4.

TABLE 2

ΔH_{S1}^{298} data. Dissolution of carbon disulphide in dioxan [a]

Run no.	Carbon disulphide		θ_R (mV)	ΔH_{S1}^{298} (kJ $mole^{-1}$)
	mg	n_R		
1	18.93	0.2487	0.120	2.13
2	22.94	0.3013	0.140	2.04
3	26.93	0.3537	0.190	2.22
4	14.97	0.1966	0.089	1.97
5	22.45	0.2949	0.165	2.35
6	23.02	0.3024	0.149	2.10
7	20.16	0.2648	0.121	1.91
8	27.49	0.3611	0.200	2.38

[a] $\Delta H_{S1}^{298} = 2.14 \pm 0.12$ kJ $mole^{-1}$ for the reaction $CS_2(l) \rightarrow CS_2(soln)$

TABLE 3

Heat capacity data. Reaction of diethylamine with carbon disulphide

Calibration no.	θ_c (mV)	V_1 (volts)	V_2 (volts)	t (sec)	Heat capacity ϵ (amp sec) $\times 10^3$
1	14.08	9.0168	8.5721	69	3.7851
2	12.48	9.0230	8.5660	60	3.7133
3	14.45	9.0162	8.5718	66	3.5275
4	19.35	9.0182	8.5708	90	3.5925
5	16.02	9.0171	8.5706	75	3.6155
6	15.45	9.0170	8.5721	69	3.4496

Determination of ΔH_{S3}^{298}

Ampoules were loaded with ground diethylammonium diethyldithiocarbamate (0.01—0.06 mmoles) and were broken into 40 cm^3 of dioxan. Calorimetric data leading to ΔH_{S3}^{298} are recorded in Tables 5 and 6.

Determination of the standard heat of formation of diethylammonium diethyldithiocarbamate

Substituting ΔH_{S1}^{298}, ΔH_{S2}^{298} and ΔH_{S3}^{298} in eqn. (1) yields $\Delta H_r^{298} = -81.1 \pm 3.2$ kJ mole^{-1} $(C_2H_5)_2NH_2S_2CN(C_2H_5)_2$.

The following standard enthalpies of formation were taken from the literature. Carbon disulphide: 89.66 (±0.71) [12]; diethylamine: −103.68 (±1.21) [13] kJ mole^{-1}, respectively. Hence ΔH_f^0 $(C_2H_5)_2NH_2S_2CN(C_2H_5)_2 = -198.8 \pm 4.1$ kJ mole^{-1}.

The enthalpy of sublimation of diethylammonium diethyldithiocarbamate has been reported as 111.8 ± 3.0 kJ mole^{-1} [3] and thus the enthalpy of formation of gaseous diethylammonium diethyldithiocarbamate is −87.0 ± 4.6 kJ mole^{-1}.

TABLE 4

ΔH_{S2}^{298} data. Reaction of diethylamine with carbon disulphide [a]

Run no.	Diethylamine		θ_R (mV)	ΔH_{S2}^{298} (kJ mole^{-1})
	mg	n_R		
1	31.669	0.43299	13.05	−114.08
2	24.235	0.33135	10.40	−116.55
3	30.608	0.41849	13.45	−113.37
4	44.086	0.60276	18.70	−111.45
5	37.415	0.51155	16.10	−113.79
6	33.156	0.45332	14.90	−113.38

[a] $\Delta H_{S2}^{298} = -113.8 \pm 1.4$ kJ mole^{-1} = $(CH_3CH_2)_2NH$, for the reaction

$CS_2(soln) + 2(CH_3CH_2)_2NH(l) \rightarrow (CH_3CH_2)_2NH_2 \cdot S_2CN(CH_2CH_3)_2(soln)$

TABLE 5

Heat capacity data. Dissolution of diethylammonium diethyldithiocarbamate in dioxan

Calibration no.	θ_c (mV)	V_1 (volts)	V_2 (volts)	t (sec)	Heat capacity ϵ (amp sec) $\times 10^3$
1	2.37	2.9341	2.7785	120	4.1249
2	0.88	2.9344	2.7786	45	4.1665
3	1.20	2.9340	2.7786	60	4.0733
4	1.18	2.9339	2.7785	60	4.1421
5	1.30	2.9341	2.7786	66	4.1362

TABLE 6

ΔH_{S3}^{298} data. Dissolution of diethylammonium diethyldithiocarbamate in dioxan[a]

Run no.	Diethylammonium diethyldithiocarbamate		θ_R (mV)	ΔH_{S3}^{298} (kJ mole^{-1})
	mg	n_R		
1	13.46	0.060518	2.10	−143.14
2	6.57	0.029540	1.04	−146.69
3	3.15	0.014163	0.50	−143.80
4	6.46	0.029046	1.00	−142.60
5	5.87	0.026393	0.93	−145.75

[a] Molar mass of $(CH_3CH_2)_2NH_2 \cdot S_2CN(CH_2CH_3)_2$ = 222.406 g mole^{-1}. $\Delta H_{S3}^{298} = -144.40 \pm 1.6$ kJ mole^{-1} for the reaction

$(CH_3CH_2)_2NH \cdot S_2CN(CH_3CH_2)_2(c) \rightarrow (CH_3CH_2)_2NH \cdot S_2CN(CH_2CH_3)_2(soln)$

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