Note

SUBLIMATION ENTHALPY OF Ni(II) AND Cu(II) DIETHYLDITHIOCARBAMATE AND DIETHYLAMMONIUM DIETHYLDITHIOCARBAMATE BY THE SUBLIMATION BULB TECHNIQUE

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The sublimation bulb technique for the indirect determination of the sublimation enthalpy of compounds in the solid state was first suggested by Melia and Merrifield [1] and was subsequently modified by Chickos [2]. Essentially, the vapour pressure of the compound is measured indirectly using a spectrophotometric method, a concept which Chickos [2] extended by employing quantitative infrared and ultraviolet spectroscopy and gas chromatographic analysis. The principal advantages of the sublimation bulb technique for the measurement of static vapour pressures are that complete outgassing of the sample is unnecessary and the precision associated with this technique appears to be considerably greater than that associated with the isoteniscope [3], spoon gauge [4] or transpiration techniques [5].

This note reports the enthalpy of sublimation of two simple metal dithiocarbamate complexes and one dialkylammonium dialkyldithiocarbamate salt. The volatility characteristics of the latter are unexpected in view of the demonstrated [6] salt-like behaviour of this family of compounds.

EXPERIMENTAL

A sublimation bulb of similar design to that of Melia and Merrifield [1] and Chickos [2] was employed except that the sample chamber was positioned such that sample and top surface of the bulb were maintained at the same temperature whilst the bulk of the bulb was sunk deeper into the oil thermostat bath thus reducing adsorption of sample onto the bulb wall. Such relative positioning of the sample chamber and bulb allowed sample chamber and vacuum line taps to be operated without removal of the apparatus from the thermostat, thereby ensuring no disturbance of the established solid—vapour equilibrium. The bulb volume (1085.8 ± 0.2 cm³) was determined by recording the difference in mass of the bulb when empty and when filled with degassed distilled water at 298 K. At the higher temperatures employed in the vapour pressure measurements, allowance was made for bulb expansion (0.01 cm³ deg⁻¹). The thermostat bath contained Shell Ondina 33 oil (flash point 195°C). Temperature control (±0.05°C) was effected using a Utah Electronics H2-7 temperature controller in conjunction with a 2000

TABLE 1

Melting point and microanalysis data for dithiocarbamate compounds

Compound	Melting point (°C)	Carbon (%)		Hydrogen (%)		Nitrogen (%)		Sulphur (%)	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Ni[S$_2$CN(CH$_2$CH$_3$)$_2$]$_2$	234—236	33.8	34.0	5.7	5.8	7.9	7.8	36.1	35.9
Cu[S$_2$CN(CH$_2$CH$_3$)$_2$]$_2$	190—192	33.4	33.7	5.6	5.7	7.8	7.8	35.7	35.6
(C$_2$H$_5$)$_2$NH$_2$S$_2$CN(C$_2$H$_5$)$_2$	83—84	48.6	48.5	i0.0	9.7	12.6	12.5	28.8	28.6

ohm thermistor. The bath heater consisted of a nichrome wire heater contained in a glass helix filled with Ondina oil. Temperatures were measured using calibrated Zum Ultra, mercury in glass, 170 mm, fixed immersion thermometers. The Melia—Merrifield standard experimental procedure [1] was employed and sample solutions were analysed using a Perkin-Elmer Model DK2A spectrophotometer.

In all cases, the measured absorbances were converted to sublimation pressures by substitution of the measured values in the equation

$$P = \frac{62.365A\,V_s T}{V_T \epsilon d} \tag{1}$$

where P is in mm Hg, A is the absorbance of the extract at a selected wavelength, V_s is the volume of solvent introduced into the bulb, T is the temperature of measurement in K, V_T is the volume of the bulb at the temperature of measurement, ϵ is the molar extinction coefficient of the sample under investigation at the selected wavelength (determined in calibration experiments) and d is the path length in cm.

A least-squares treatment of the vapour pressure—temperature data was applied to compute values of the constants A and B in the linear equation

$$\log_{10} P = A - BT^{-1}$$

and hence ΔH_{sub} for the test compound.

The dithiocarbamate compounds were synthesised by well-established procedures [6,7] and were purified by repeated sublimation. Relevant melting point and microanalysis data are given in Table 1.

RESULTS AND DISCUSSION

Diethylammonium diethyldithiocarbamate

The instability of this compound in a wide variety of organic solvents necessitated dissolution of the condensed vapour in a Cu^{2+}—dimethylformamide standard solution and subsequent spectrophotometric analysis of diethylammonium diethyldithiocarbamate as bis(diethyldithiocarbamato)-Cu(II). The selected wavelength was the 345 nm ($\epsilon \simeq 12,000$) metal—ligand charge transfer band. The relevant vapour pressure—temperature data are recorded in Table 2 and Fig. 1 and are described by the equation $\log_{10} P = 17.858 - 5480.7T^{-1}$ yielding $\Delta H_{sub}(C_2H_5)_2NH_2S_2CN(C_2H_5)_2 = 111.8 \pm 3.0$ kJ mole^{-1}.

Bis(diethyldithiocarbamato)nickel(II)

The condensed vapour was dissolved in Analar chloroform and analysed spectrophotometrically using the selected wavelength of 388 nm ($\epsilon \simeq 6,000$) metal—ligand charge transfer band. The relevant vapour pressure—temperature data are recorded in Table 3 and Fig. 2 and are described by the equation $\log_{10} P = 9.458 - 5358.8T^{-1}$ yielding $\Delta H_{sub}[(C_2H_5)_2NCS_2]_2Ni = 102.6 \pm 1.5$ kJ mole^{-1}.
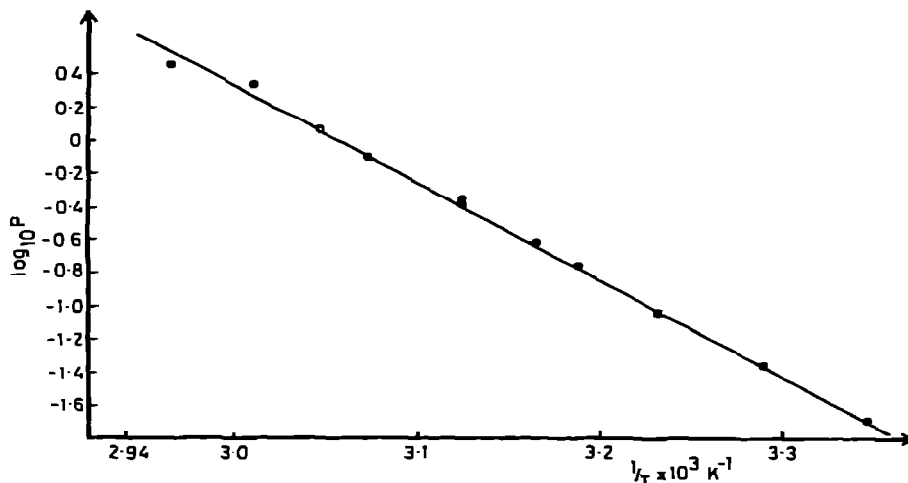
Fig. 1. Plot of $\log_{10}P$ vs. $1/T$ for diethylammonium diethyldithiocarbamate.

Bis(diethyldithiocarbamato)copper(II)

The condensed vapour was dissolved in Analar dimethylformamide and analysed spectrophotometrically using the selected wavelength of 435 nm ($\epsilon \simeq 12,000$) metal—ligand charge transfer band. The relevant vapour pressure—temperature data are recorded in Table 4 and Fig. 3 and are described by the equation $\log_{10}P = 11.602 - 6071.8T^{-1}$ yielding $\Delta H_{sub}[(C_2H_5)_2\text{-}NCS_2]_2Cu = 116.2 \pm 1.3$ kJ mole^{-1}.

Published ΔH_{sub} data for nickel and copper diethyldithiocarbamate complexes as derived from isoteniscopic measurements over the temperature range 25—220°C are 61.1 ± 1.7 and 87 ± 1.7 kJ mole^{-1}, respectively [8]. It is apparent that the large discrepancy between previous and present data is due predominantly to the very low vapour pressures of these complexes

TABLE 2

Vapour pressure—temperature data for diethylammonium diethyldithiocarbamate

Run no.	Temperature (K)	$1/T$ (K^{-1})	Pressure (mmHg)	$\log_{10}P$
1	298.9	0.003346	0.01998	—1.6994
2	304.0	0.003289	0.04344	—1.3621
3	309.4	0.003232	0.09062	—1.0428
4	313.7	0.003188	0.1734	—0.7610
5	315.9	0.003166	0.2408	—0.6182
6	319.9	0.003126	0.4121	—0.3850
7	320.0	0.003125	0.4261	—0.3704
8	325.4	0.003073	0.7887	—0.1031
9	328.1	0.003048	1.1783	0.0712
10	332.1	0.003011	2.1132	0.3251
11	337.1	0.0029 -6	2.8375	0.4529

TABLE 3

Vapour pressure—temperature data for bis(diethyldithiocarbamato) nickel (II)

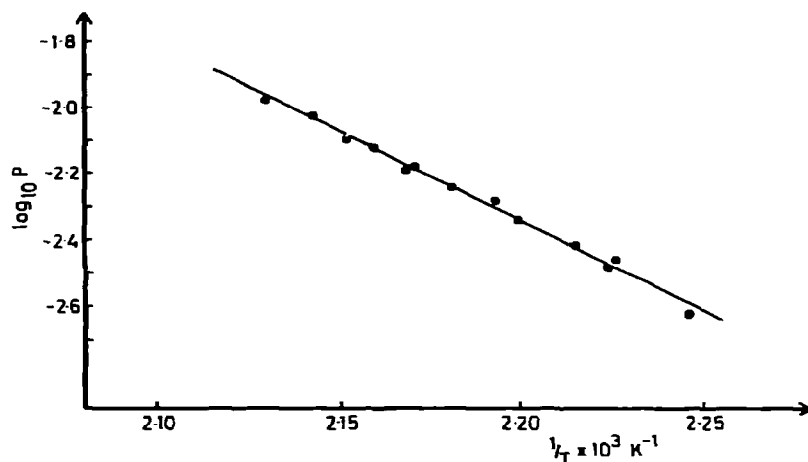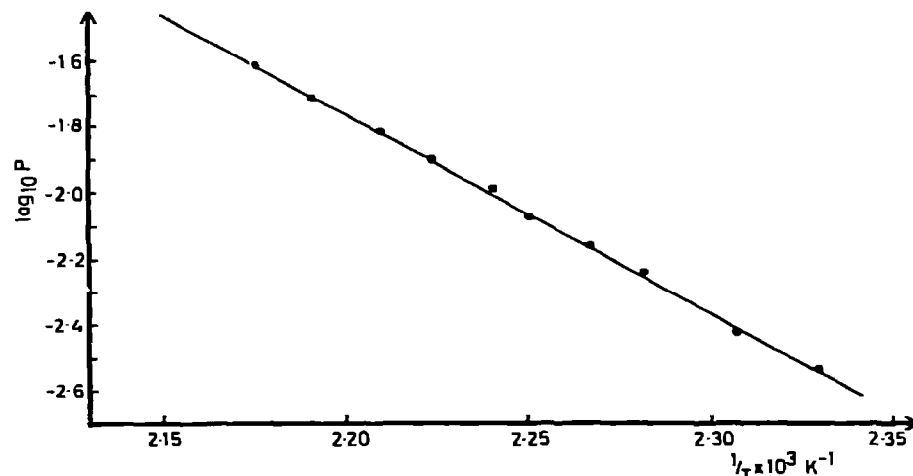| Run no.	Temperature (K)	$1/T$ (K^{-1})	Pressure (mmHg)	$\log_{10}P$
1	445.3	0.002246	0.002458	—2.6094
2	449.2	0.002226	0.003597	—2.4441
3	449.7	0.002224	0.003406	—2.4678
4	451.1	0.002215	0.003955	—2.4029
5	454.7	0.002199	0.004707	—2.3273
6	456.3	0.002193	0.005353	—2.2714
7	458.6	0.002181	0.005883	—2.2304
8	460.6	0.002171	0.006827	—2.1658
9	461.2	0.002168	0.006649	—2.1772
10	463.0	0.002160	0.007692	—2.1140
11	464.8	0.002152	0.008245	—2.0838
12	466.7	0.002143	0.009693	—2.0135
13	469.5	0.002130	0.010680	—1.9714

Fig. 2. Plot of $\log_{10}P$ vs. $1/T$ for bis(diethyldithiocarbamato)nickel(II).

Fig. 3. Plot of $\log_{10}P$ vs. $1/T$ for bis(diethyldithiocarbamato)copper(II).

TABLE 4

Vapour pressure—temperature data for bis(diethyldithiocarbamato) copper (II)

Run no.	Temperature (K)	1/T (K^{-1})	Pressure (mmHg)	$\log_{10}P$
1	429.3	0.002329	0.002936	−2.5322
2	433.4	0.002307	0.003771	−2.4235
3	438.2	0.002282	0.005672	−2.2463
4	441.1	0.002267	0.006916	−2.1601
5	444.4	0.002250	0.008352	−2.0782
6	446.2	0.002241	0.010400	−1.9830
7	449.6	0.002224	0.012710	−1.8959
8	452.4	0.002210	0.015280	−1.8159
9	456.4	0.002191	0.019500	−1.7100
10	459.5	0.002176	0.024500	−1.6108

resulting in large uncertainties associated with their isoteniscopic measurement coupled with the difficulty of complete outgassing of the samples for isoteniscopic study. The present data are in reasonable agreement with recent DSC data [9]. $\Delta H_{sub} = 98.8 \cdot 6.0$ kJ mole^{-1} and $\Delta H_{sub} = 104.0$ 8.0 kJ mole^{-1} measured at 507—650 K and 455—597 K, respectively.

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