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ENTHALPIES OF DECOMPOSITION OF DIALKYLAMMONIUMDIALKYLDITHIOCARBAMATES (ALKYL = ETHYL, n-PROPYL, i-PROPYL, i-BUTYL)

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ABSTRACT

Comparison of the enthalpy of sublimation from direct calorimetric measurement with that derived from vapour pressures as functions of temperature has shown that dialkylammoniumdialkyldithiocarbamates decompose according to

$R_2NH_2S_2CNR_2(c) = R_2NH(g) + HS_2CNR_2(g)$

From the enthalpies of decomposition at 298.15 K and literature values of $\Delta_f H_m^\ominus(R_2NH_2S_2CNR_2,c)$ and $\Delta_f H_m^\ominus(R_2NH,g)$, a value of $\Delta_f H_m^\ominus(HS_2CNR_2,g)$ was derived.

R	$\Delta_{dec} H_m^\ominus$ (kJ mol^{-1})	$\Delta_f H_m^\ominus(HS_2CNR_2,g)$ (kJ mol^{-1})
Et	209.9 ± 2.8	33.2 ± 3.8
n-Pr	221.9 ± 3.6	-15.2 ± 3.9
i-Pr	187.7 ± 1.0	-17.9 ± 1.7
i-Bu	217.0 ± 1.8	-67.6 ± 2.4

Application of a group additivity scheme to $\Delta_f H_m^\ominus(HS_2CNR_2,g)$ shows a large steric hindrance for R = i-Pr.

INTRODUCTION

Dialkylammoniumdialkyldithiocarbamates $(R_2NH_2)^+(S_2CNR_2)^-$ provide an excellent source of the dialkyldithiocarbamate ligand (S_2CNR_2) required for the preparation of metal dialkyldithiocarbamates. The enthalpy of sublimation of $Et_2NH_2S_2CNEt_2$ ($\Delta_{sub} H_m^\ominus = 111.8 \pm 3.0$ kJ mol^{-1}) was reported by Cavell et al. [1], determined from the vapour pressure as a function of temperature. The vapour pressures were measured using a sublimation bulb technique, i.e. the number of moles of $Et_2NH_2S_2CNEt_2(g)$ contained in a measured volume, in equilibrium with the solid, were determined by chemical analysis and the corresponding vapour pressure was

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derived assuming ideal gas behaviour. The vapour pressure–temperature data reported can be represented by $\log_{10} p$ (mm Hg) = 17.858 – 5840.7T^{-1}, hence at 298.15 K, $\Delta_{\text{sub}}G_{\text{m}}^{\ominus} = 26.33$ kJ mol^{-1} and this leads to an extraordinarily large value for the standard entropy of sublimation, $\Delta_{\text{sub}}S_{\text{m}}^{\ominus} = 287$ J K^{-1} mol^{-1}, suggesting that the process studied was not a simple sublimation. $(Et_2NH_2)^+(S_2CNEt_2)^-$ may be regarded as a substituted ammonium salt and in common with other ammonium salts it is improbable that it would exist in an undissociated form in the gaseous state.

The compounds $R_2NH_2S_2CNR_2$(c) can be purified using techniques normally applied to the sublimation of volatile organic compounds. If we use the term "sublimation" for the process in which a molecule is transferred unchanged between the solid and gaseous phases, then we may refer to the process in which the molecule is transferred but is not unchanged as an "apparent sublimation".

In this paper we report the enthalpies of "apparent sublimation" measured by microcalorimetry for $R_2NH_2S_2CNR_2$, R = Et, n-Pr, i-Pr and i-Bu. These values were compared with those derived by applying the Clausius–Clapeyron equation to the vapour pressures measured as functions of temperature. The vapour pressures were measured using a Knudsen cell placed in the microcalorimeter. The comparison has shown that $R_2NH_2S_2CNR_2$ is dissociated in the gaseous phase into two molecules, presumably R_2NH(g) and HS_2CNR_2(g). The molar enthalpies of formation of $R_2NH_2S_2CNR_2$(c), R = Et, n-Pr, i-Pr, n-Bu, and i-Bu have been reported [2], hence the enthalpies of decomposition permitted the derivation of $\Delta_{\text{f}}H_{\text{m}}^{\ominus}(HS_2CNR_2,\text{g})$.

EXPERIMENTAL

Materials

The $R_2NH_2S_2CNR_2$ compounds were prepared as reported by Cavell et al. [3] by adding an excess of carbon disulphide to a 25% (v/v) solution of the appropriate dialkylamine, R_2NH, in acetone held at temperatures < 10 °C in an ice-bath. The solid products were washed with light petroleum and recrystallized from acetone–light petroleum mixtures, except for the ethyl compound when diethylether was used. The products were dried in vacuo and stored in the dark.

Microcalorimeter

The Calvet high temperature microcalorimeter (0–1000 ° C, Seteram, Lyon, France) was used. This is a twin conduction microcalorimeter of maximum sensitivity 5 μW. The vacuum-sublimation drop microcalorimetric method

TABLE 1

Enthalpy of "apparent sublimation" of $(n\text{-Pr})_2NH_2S_2CN(n\text{-Pr})_2$ [M (g mol^{-1}) = 278.5214]

T (K)	mass (mg)	Area (unit)	ΔH_{obs} (kJ mol^{-1})	$[H(T)-H(298)](g)$ (kJ mol^{-1})	$\Delta H(298\ K)$ (kJ mol^{-1})
376	2.177	1770	262.23	32.79	229.44
376	2.593	2097	260.83	32.79	228.04
376	2.288	1813	255.57	32.79	222.78
376	2.357	1829	250.28	32.79	217.49
					Mean 224.4 ± 5.4
387	4.621	3668	254.46	37.42	217.04
387	4.348	3507	258.57	37.42	221.15
387	5.194	4096	252.81	37.42	215.39
387	2.269	1850	261.38	37.42	223.96
					Mean 219.4 ± 3.9

[4] was used to measure the enthalpies of "apparent sublimation". Samples of about 4 mg of $R_2NH_2S_2CNR_2(c)$ contained in small thin glass capillary tubes sealed at one end were dropped at room temperature into the hot reaction vessel in the microcalorimeter held at a constant temperature between 366 and 387 K, and were then removed from the calorimeter by applying a vacuum. The thermal corrections for the glass capillary tubes were determined in separate experiments, and were minimized by dropping tubes of nearly equal mass, to within ±10 μg into the twin calorimeter cells. The calorimeter was calibrated in situ for these experiments by making use of the reported enthalpy of sublimation of naphthalene [5]. The quantity measured in the calorimeter was $[H_m^\ominus(g,\ T) - H_m^\ominus(c,\ 298.15\ K)]$ and, to correct to 298.15 K $[H_m^\ominus(g,\ T) - H_m^\ominus(g,\ 298.15\ K)]$ was required. These correction terms, calculated assuming the gas to be an equimolar mixture of R_2NH and HS_2CNR_2, were relatively large, between 12 and 20% of the observed enthalpy change, and the methods used for their estimation are described in the appendix. Detailed results for $(n\text{-Pr})_2NH_2S_2CN(n\text{-Pr})_2$ are given in Table 1, where at 376 K the calorimeter sensitivity is $k = 1.158$ mJ area unit^{-1} and at 387 K, $k = 1.151$ mJ area unit^{-1}. In accord with normal thermochemical practice, all the experimental uncertainties quoted are twice the standard deviation of the mean. The molar enthalpies of "apparent sublimation" of $R_2NH_2S_2CNR_2$ are listed in Table 2 together with the weighted mean values.

Vapour pressure measurements

The Knudsen cell made of Pyrex is shown in Fig. 1, inside the steel calorimeter vessel which was placed within the microcalorimeter thermopile detectors. The effusion hole was approx. 0.3 mm in diameter in a platinum

TABLE 2

Enthalpy of "apparent sublimation" of $R_2NH_2S_2CNR_2$

R	M (g mol^{-1})	T (K)	No. of expts.	ΔH_{obs} (kJ mol^{-1})	$[H(T)-H(298)](g)$ (kJ mol^{-1})		$\Delta H(298\ K)$ (kJ mol^{-1})
Et	222.4142	378	4	234.0 ± 1.9	25.1		208.9 ± 1.9
		387	12	240.4 ± 3.0	27.9		212.5 ± 3.0
						Weighted mean	209.9 ± 2.8
n-Pr	278.5214	376	4	257.2 ± 5.4	32.8		224.4 ± 5.4
		387	4	256.8 ± 3.9	37.4		219.4 ± 3.9
						Weighted mean	221.9 ± 3.6
i-Pr	278.5214	376	10	220.9 ± 1.0	32.8		188.1 ± 1.0
		387	5	224.1 ± 6.8	37.4		186.7 ± 6.8
						Weighted mean	187.7 ± 1.0
i-Bu	334.6286	376	3	258.6 ± 2.3	40.0		218.6 ± 2.3
		387	4	262.7 ± 2.7	46.5		215.9 ± 2.0
						Weighted mean	217.0 ± 1.8

sheet of 0.01 mm thickness. On applying high vacuum to the Knudsen cell, heat was absorbed to sublime solid to replace the vapour lost by effusion. The system was allowed to attain a steady-state when the rate of heat adsorbed was directly proportional to the rate of effusion. As the calorimeter was operated between 292 and 330 K, at temperatures below those previously used for calibration and the effusion hole area was not measured accurately, then absolute vapour pressures could not be derived reliably. The vapour pressures were measured relative to those of naphthalene [6], as in this temperature range, naphthalene vapour pressures are of the same order of magnitude as those of $R_2NH_2S_2CNR_2$. Although the absolute values of vapour pressures derived by this procedure were not of the accuracy normally attainable by the Knudsen method, the change in vapour pressure with temperature was determined reliably.

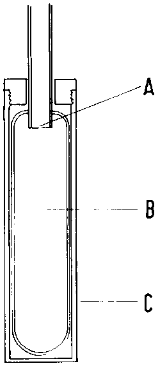


Fig. 1. Knudsen cell. A, effusion hole; B, Pyrex vessel; C, microcalorimeter cell.

TABLE 3

Vapour pressure–temperature data for $Et_2NH_2S_2CNEt_2$

T (K)	p (mm Hg)	$10^3\,(T^{-1})$ (K^{-1})	ln p (mm Hg)
300.3	0.026	3.3300	−3.6400
311.0	0.115	3.2154	−2.1603
320.5	0.393	3.1201	−0.9341

TABLE 4

Vapour pressure–temperature data for $(n\text{-}Pr)_2NH_2S_2CN(n\text{-}Pr)_2$

T (K)	p (mm Hg)	$10^3\,(T^{-1})$ (K^{-1})	ln p (mm Hg)
309.5	0.067	3.2310	−2.7000
317.5	0.189	3.1496	−1.6657
325.5	0.569	3.0722	−0.5634
330.6	1.173	3.0248	0.1596

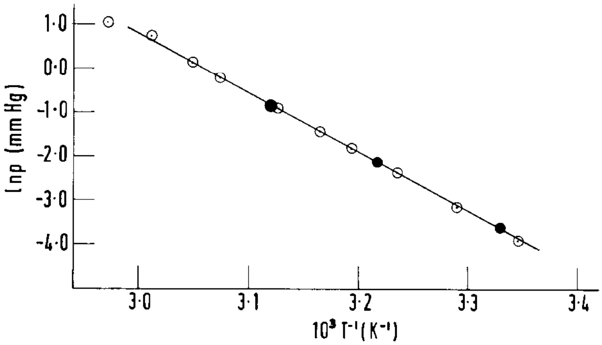


Fig. 2. ln p (mm Hg) vs. T^{-1} for $Et_2NH_2S_2CNEt_2$. ○, Cavell et al. [1]; ●, this work.

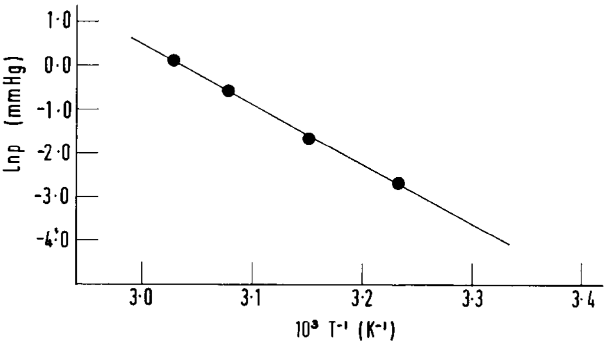


Fig. 3. ln p (mm Hg) vs. T^{-1} for $(n\text{-}Pr)_2NH_2S_2CN(n\text{-}Pr)_2$.

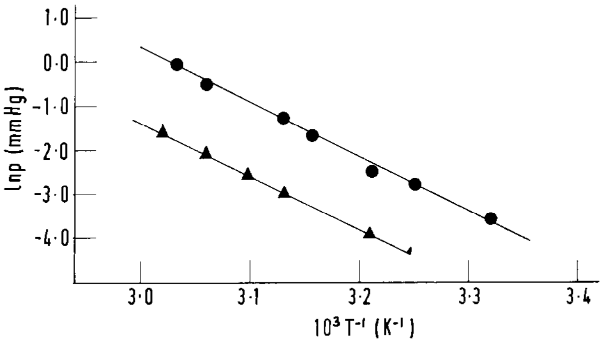


Fig. 4. ln p (mm Hg) vs. T^{-1}. ●, $(i\text{-}Pr)_2NH_2S_2CN(i\text{-}Pr)_2$; ▲, $(i\text{-}Bu)_2NH_2S_2CN(i\text{-}Bu)_2$.

TABLE 5

Vapour pressure–temperature data for $(i\text{-}Pr)_2NH_2S_2CN(i\text{-}Pr)_2$

T (K)	p (mm Hg)	10^3 (T^{-1}) (K^{-1})	ln p (mm Hg)
301.2	0.028	3.3200	−3.5792
307.6	0.057	3.2509	−2.8582
311.2	0.074	3.2134	−2.6058
317.2	0.188	3.1526	−1.6724
319.4	0.420	3.1309	−0.8673
326.7	0.565	3.0609	−0.5713
330.2	1.001	3.0285	0.0010

TABLE 6

Vapour pressure–temperature data for $(i\text{-}Bu)_2NH_2S_2CN(i\text{-}Bu)_2$

T (K)	p (mm Hg)	10^3 (T^{-1}) (K^{-1})	ln p (mm Hg)
311.0	0.018	3.2154	−4.0400
319.4	0.058	3.1309	−2.8439
323.0	0.092	3.0960	−2.3908
326.8	0.161	3.0600	−1.8238
331.2	0.255	3.0193	−1.3657

TABLE 7

Constants A and B in ln $p = A - BT^{-1}$; ΔH(apparent sublimation) from vapour pressures, from calorimetry and their ratio

R	A	B	ΔH(app. sub.) vap, pressure (kJ mol^{-1})	ΔH(app. sub.) calorimeter (kJ mol^{-1})	$\frac{\Delta H\text{(calorimeter)}}{\Delta H\text{(vap. press.)}}$
Et	41.120	13349	111.8 ± 3.0	209.9 ± 2.8	1.877 ± 0.073
n-Pr	42.037	13858	115.2 ± 5.1	221.9 ± 3.6	1.926 ± 0.122
i-Pr	38.140	12598	104.7 ± 9.2	187.7 ± 1.0	1.793 ± 0.179
i-Bu	40.302	13786	114.6 ± 5.4	217.0 ± 1.8	1.893 ± 0.111

Table 3 lists the vapour pressure–temperature data obtained for $Et_2NH_2S_2CNEt_2$, and these data together with those reported by Cavell et al. [1] are plotted in Fig. 2: the agreement between the two sets of measurements is excellent. The vapour pressure–temperature data for $R_2NH_2S_2CNR_2$ and the curves of ln p (mm Hg) vs. 10^3 T^{-1} are given for R = n-Pr, Table 4, Fig. 3; for R = i-Pr, Table 5, Fig. 4; and for R = i-Bu, Table 6, Fig. 4. The vapour pressure–temperature data were represented by the Clausius–Clapeyron equation, $\ln p = A - BT^{-1}$, hence ΔH(apparent sublimation) = $8.3141B$ J mol^{-1}. Table 7 lists A and B for each compound together with ΔH(apparent sublimation) derived from the vapour pressure measurements. Table 7 gives also the mean values of ΔH(apparent sublimation) determined calorimetrically. The ratio ΔH(calorimetric)/ΔH(vapour pressure) for each compound is close to two, demonstrating that $R_2NH_2S_2CNR_2$ dissociates in the gaseous phase to two molecules. Mass spectroscopic analyses of the vapours were consistent with the composition $R_2NH(g) + HS_2CNR_2(g)$.

DISCUSSION

The enthalpy of the decomposition

$$R_2NH_2S_2CNR_2(c) = R_2NH(g) + HS_2CNR_2(g)$$

is given by the calorimetric measurement of the enthalpy of "apparent sublimation"; the enthalpy from the vapour pressure measurements may be regarded as confirming the nature of the decomposition. The molar enthalpies of formation of $R_2NH_2S_2CNR_2(c)$ have been reported [2] and with $\Delta_f H_m^\ominus(R_2NH,g)$ [7], $\Delta_f H_m^\ominus(HS_2CNR_2,g)$ was derived: the values are listed in Table 8.

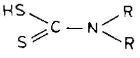
Assuming the structure of HS_2CNR_2 to be  $\mathrm{(HS)(S{=})C{-}NR_2}$ the group method of Benson [8] may be applied to these compounds with the following values, in kJ mol^{-1}, for the group contributions to $\Delta_f H_m^\ominus(g)$: [C–(N)(S)(SH)] = 63.16, [N–(C)$_3$] = 108.83, [C–(N)(C)(H)$_2$] = −28.86, [C–(N)(C)$_2$(H)] =

TABLE 8

Derived molar values for $HS_2CNR_2(g)$

R	$\Delta_f H_m^\ominus(R_2NH_2S_2CNR_2,c)$ (kJ mol^{-1})	ΔH_{dec} (kJ mol^{-1})	$\Delta_f H_m^\ominus(R_2NH,g)$ (kJ mol^{-1})	$\Delta_f H_m^\ominus(HS_2CNR_2,g)$ (kJ mol^{-1})		
				Experimental	Calculated	Δ
Et	−249.2±2.2	209.9±2.8	−72.5±1.2 [7]	33.2±3.8	29.6	−3.6
n-Pr	−353.2±1.3	221.9±3.6	−116.1±0.5 [7]	−15.2±3.9	−11.6	3.6
i-Pr	−349.6±1.3	187.7±1.0	−144.0±0.5 [7]	−17.9±1.7	−34.8	16.9
i-Bu	−463.8±1.4	217.0±1.8	−179.2±0.7 [7]	−67.6±2.4	−69.7	−2.1

-18.72, $[C\text{–}(C)(H)_3] = -42.34$, $[C\text{–}(C)_2(H)_2] = -20.59$, $[C\text{–}(C)_3(H)] = -7.32$. The group $[C\text{–}(N)(S)(SH)]$ is a composite consisting of $\{[C\text{–}(N)(S)(SH)] + [S\text{–}(C)] + [S\text{–}(H)(C)]\}$ and includes any steric terms due to interaction of the $[HS_2CN<]$ group with n-alkyl chains; its value was derived as the mean from $\Delta_f H_m^{\ominus}(g)$ for HS_2CNEt_2 and $HS_2CN(n\text{-}Pr)_2$: the remaining group parameters were taken from Cox and Pilcher [9].

The calculated values are given in Table 8 and agree with the experimental values within the limits of experimental error except for $HS_2CN(i\text{-}Pr)_2$, where the sign of the deviation indicates steric hindrance in this molecule. Enthalpies of formation of molecules of closely similar structures are not available for comparison but we can compare with alkanes derived by replacing the $[HS_2CN<]$ group with $[CH_3\text{-}CH<]$. The steric strain-energies in these corresponding alkanes are according to Skinner [10], in kJ mol^{-1}, for R = Et, 4.0; R = n-Pr, 4.0; R = i-Pr, 17.4; and for R = i-Bu, an estimated value of 2.8. Hence the derived enthalpies of formation of $HS_2CNR_2(g)$ do fall into an obvious pattern.

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APPENDIX

Estimation of $[H_m^{\ominus}(g, T) - H_m^{\ominus}(g, 298.15\ K)]$

The gaseous product was assumed to be an equimolar mixture of R_2NH and HS_2CNR_2. To estimate $H(T) - H(298.15\ K)$, a group additivity method based on the data reported by Stull et al. [5] was used. Experimental data are available for Et_2NH and for the other R_2NH, values were estimated by applying increments derived from alkanes to the value for Et_2NH, e.g. for $(n\text{-}Pr)_2NH$

$$[H(T) - H(298.15\ K)][(n\text{-}Pr)_2NH,(g)]$$
$$= [H(T) - H(298.15\ K)][Et_2NH(g) + 2n\text{-}C_4H_{10}(g) - 2C_3H_8(g)]$$

No experimental data are available for $HS_2CNR_2(g)$ and few data for compounds containing (C=S). The average increment for changing (C=O) to (C=S), Δ_O^S, was calculated from the data given in Table A1. The estimate for HS_2CNEt_2 was made using the equation

$$[H(T) - H(298.15\ K)](HS_2CNEt_2,g) = [H(T) - H(298.15\ K)]$$
$$[(C_2H_5)_3N(g) + (CH_3)_2CO(g) + C_2H_5SH(g) - 2C_3H_8(g) + \Delta_O^S]$$

TABLE A1

$H_m^\ominus(g, T) - H_m^\ominus(g, 298.15\ K)$ for Δ_O^S (kJ mol^{-1})

T (K)	CO_2	COS	CS_2	Δ_O^S
300	0.08	0.08	0.13	0.04
400	4.02	4.48	4.85	0.42
500	8.33	9.20	9.96	0.82

TABLE A2

$H_m^\ominus(g, T) - H_m^\ominus(g, 298.15\ K)$ [5] (kJ mol^{-1})

T (K)	C_2H_8	n-C_4H_{10}	$(C_2H_5)_3$-N	$(CH_3)_2$-CO	C_2H_5-SH	$(C_2H_5)_2$-NH	CH_3CH-$(CH_3)_2$	C_2H_5-$CH(CH_3)_2$
300	0.17	0.21	0.33	0.17	0.17	0.25	0.21	0.25
400	8.58	11.30	18.62	8.54	8.24	13.35	11.30	13.89
500	18.95	24.31	41.00	18.58	17.74	29.37	25.02	30.67

TABLE A3

$H_m^\ominus(g, T) - H_m^\ominus(g, 298.15\ K)$ estimated values in kJ mol^{-1}

T (K)	(n-Pr)$_2$-NH	(i-Pr)$_2$-NH	(i-Bu)$_2$-NH	HS_2CNEt_2	HS_2CN-(n-Pr)$_2$	HS_2CN-(i-Pr)$_2$	HS_2CN-(i-Bu)$_2$
300	0.33	0.33	0.42	0.38	0.46	0.46	0.54
400	18.79	18.79	23.97	18.66	24.10	24.10	29.29
500	41.34	41.34	52.80	40.25	52.22	52.22	63.68

and for the other HS_2CNR_2 compounds, the values were estimated by applying increments derived from alkanes to the value for HS_2CNEt_2. The basic data used are given in Table A2 and the derived estimates used to calculate by interpolation $[H(T) - H(298.15\ K)]$ for the gaseous phase resulting from the decomposition of $R_2NH_2S_2CNR_2(c)$ are given in Table A3.

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