Thermochimica Acta, 6 (1973) 269–274
© Elsevier Scientific Publishing Company, Amsterdam – Printed in Belgium

THE THERMAL DECOMPOSITION OF TRANSITION-METAL COMPLEXES CONTAINING HETEROCYCLIC LIGANDS

I. BENZOTHIAZOLE COMPLEXES

C. T. MORTIMER AND JANICE L. McNAUGHTON
Chemistry Department, University, Keele, Staffordshire (England)

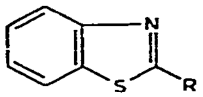
(Received 3 November 1972)

ABSTRACT

Enthalpies of the decomposition reactions $MX_2L_2(c) \rightarrow MX_2(c) + 2L(g)$, where M is Mn, Co, Ni, Cu, or Cd, X is Cl and/or Br, and L is benzothiazole or 2-methylbenzothiazole have been measured by use of a differential scanning calorimeter. Specific heats and enthalpies of sublimation of some of the complexes have been obtained.

INTRODUCTION

In previous papers[1–5] we have reported enthalpies of thermal decomposition of complexes of the type MX_2L_n, where the ligands, L, had the common feature of a N atom bonded within a six-membered unsaturated ring, e.g. pyridine, quinoline, pyrazine. This paper extends the work to complexes in which the N atom is bonded within a five-membered ring in the ligands benzothiazole, BT, and 2-methylbenzothiazole, 2MeBT.



R = H, benzothiazole; R = CH_3, 2-methylbenzothiazole

The overall decomposition reaction (1) was divided into two stages, though these stages were not the same for each complex.

$$MX_2L_2(c) \rightarrow MX_2(c) + 2L(g) \quad (1)$$

$$MX_2L_2(c) \rightarrow MX_2L(c) + L(g) \quad (2)$$
$$MX_2L(c) \rightarrow MX_2(c) + L(g) \quad (3)$$

or

$$MX_2L_2(c) \rightarrow MX_2L_{\frac{3}{4}}(c) + 1\tfrac{1}{4}L(g) \quad (4)$$
$$MX_2L_{\frac{3}{4}}(c) \rightarrow MX_2(c) + \tfrac{3}{4}L(g) \quad (5)$$

or

$$MX_2L_2(c) \rightarrow MX_2L_{\frac{2}{3}}(c) + 1\tfrac{1}{3}L(g) \quad (6)$$

$$MX_2L_{\frac{2}{3}}(c) \rightarrow MX_2(c) + \tfrac{2}{3}L(g) \quad (7)$$

or

$$MX_2L_2(c) \rightarrow MX_2L_{\frac{1}{2}}(c) + 1\tfrac{1}{2}L(g) \quad (8)$$

$$MX_2L_{\frac{1}{2}}(c) \rightarrow MX_2(c) + \tfrac{1}{2}L(g) \quad (9)$$

or

$$MX_2L_2(c) \rightarrow MX_2L_{\frac{1}{3}}(c) + 1\tfrac{2}{3}L(g) \quad (10)$$

$$MX_2L_{\frac{1}{3}}(c) \rightarrow MX_2(c) + \tfrac{1}{3}L(g) \quad (11)$$

EXPERIMENTAL

The complexes were prepared by methods described previously[6,7], and purity was established by microanalysis for C, H, and N. The Perkin–Elmer differential scanning calorimeter (DSC-1) was used to measure the enthalpies of thermal decompositions in a nitrogen atmosphere, by a procedure referred to previously[1]. The scan rate was 16 K min^{-1} in all experiments and the sensitivity was 2, 4, or 8 mcal (full scale deflection)$^{-1}$ sec^{-1}. The instrument was calibrated by use of the enthalpy of fusion of indium (0.78 kcal mol^{-1}). Enthalpy changes of the following reactions were measured and the values obtained compare well with literature[1,8,9] values.

$Pb(c, foil) \rightarrow Pb(liq.)$
$\Delta H_{600} = 1.14 \pm 0.01$ kcal mol^{-1}

$CoCl_2(pyridine)_2(c, tetrahedral) \rightarrow CoCl_2(c) + 2\ pyridine\ (g)$
$\Delta H_{530} = 28.3 \pm 0.5$ kcal mol^{-1}

$CuSO_4 \cdot 5H_2O(c) \rightarrow CuSO_4 \cdot H_2O(c) + 4H_2O(g)$
$\Delta H_{375} = 51.7 \pm 0.5$ kcal mol^{-1}

$CuSO_4 \cdot H_2O(c) \rightarrow CuSO_4(c) + H_2O(g)$
$\Delta H_{500} = 16.5 \pm 0.6$ kcal mol^{-1}

Specific heat data were obtained by use of the differential scanning calorimeter according to the method described by O'Neill[10]. Enthalpies of sublimation were obtained by use of a Dupont thermal analyser according to Ashcroft's method[11].

RESULTS

Enthalpies of successive stages of the decomposition reactions are shown in Tables 1 and 2. The symbols T_i, T_p, and T_f refer to the initial, peak (where the rate of ΔH change was greatest), and final temperatures of the dissociation reaction, respectively. The enthalpies of the overall decomposition reactions (1) are shown in Table 3, where T_m is the mean of the T_p values of the two successive reactions. In all cases the

ΔH values, which refer to the temperatures T_p or T_m, are the mean of at least five experiments, and the associated uncertainties are standard deviations of the mean values.

TABLE 1

BENZOTHIAZOLE COMPLEXES: ENTHALPIES OF STEPWISE DECOMPOSITION

Complex	*Reaction*	ΔH (*kcal mol*$^{-1}$)	T_i (*K*)	T_p (*K*)	T_f (*K*)	*Weight loss* (%) *obs.*	*Weight loss* (%) *calc.*
$MnCl_2(BT)_2$	10	23.1±0.1	455	500	510	43.4±0.5	43.6
	11	12.4±0.4	540	585	595		
$CoCl_2(BT)_2$	8	[a]	485	535		49.2±1.2	50.7
	9			580	585		
$CoBr_2(BT)_2$	8	[a]	480	535		41.2±1.8	41.5
	9			570	590		
$NiCl_2(BT)_2$	10	21.8±0.6	470	515	530	54.2±0.8	56.3
	11	11.3±0.2	540	580	595		
$CuCl_2(BT)_2$	6	[a]	420	465		45.4±0.3	44.5
	7			550	565		
$CdCl_2(BT)_2$	2	17.1±0.1	405	460	480	32.6±0.3	29.8
	3	16.8±0.4	495	570	585		
$CdBr_2(BT)_2$	4	15.7±0.2	385	(420, 445)	455	29.3±0.6	31.1
	5	19.7±0.2	485	535	545		

[a] Areas of peaks were insufficiently separated to obtain values for stepwise enthalpies, but approximate weight losses established stoichiometry of intermediate compounds.

TABLE 2

2-METHYLBENZOTHIAZOLE COMPLEXES: ENTHALPIES OF STEPWISE DECOMPOSITION

Complex	*Reaction*	ΔH (*kcal mol*$^{-1}$)	T_i (*K*)	T_p (*K*)	T_f (*K*)	*Weight loss* (%) *obs.*	*Weight loss* (%) *calc.*
$CoCl_2(2MeBT)_2$	2	19.2±0.3	405	440	470	35.0±0.3	34.8
	3	20.9±0.3	500	565	580		
$CoBr_2(2MeBT)_2$	2	17.7±0.1	420	465	480	29.6±0.6	28.8
	3	20.8±0.3	520	585	590		

It is noted from Table 3 that for all of the complexes, except $CdBr_2(BT)_2$, the values of T_m lie in the narrow temperature range 505–550 K. We might expect that the Kirchoff corrections to refer the ΔH values to a common temperature within this range would be similar and small, compared with the quoted uncertainties. In the absence of specific heat data for gaseous benzothiazole and 2-methylbenzothiazole it has not been possible to make these corrections. Nevertheless, we report measurement of specific heat data for a selection of these compounds, so that the ΔH values might be referred to other temperatures, should data for the benzothiazoles become available. Values for the constants a and b in the relationship $C_p = a + bT$, together with the temperature range to which these constants refer, are shown in Table 4.

TABLE 3

ENTHALPIES OF OVERALL DECOMPOSITION REACTION (1)

Complex	ΔH *(kcal mol^{-1})*	T_m *(K)*	*Weight loss (%)*	
			obs.	*calc.*
$MnCl_2(BT)_2$	35.5 ± 0.5 $(28.5 \pm 0.7)^a$	540 $(540)^a$	56.0 ± 0.8	52.4
$CoCl_2(BT)_2$	40.2 ± 0.8 $(28.6 \pm 0.5)^c$	550 (510)	67.5 ± 0.1	67.6
$CoBr_2(BT)_2$	38.3 ± 0.4 (27.3 ± 0.9)	550 (520)	53.7 ± 0.4	55.3
$NiCl_2(BT)_2$	33.1 ± 0.8 (32.6 ± 0.2)	540 (525)	64.8 ± 0.1	67.6
$CuCl_2(BT)_2$	38.4 ± 0.7 (28.0 ± 0.7)	505 (535)	64.5 ± 1.3	66.8
$CdCl_2(BT)_2$	33.9 ± 0.5 (30.4 ± 0.5)	510 (535)	59.4 ± 0.4	59.6
$CdBr_2(BT)_2$	35.4 ± 0.4	480	49.7 ± 0.1	49.8
$CoCl_2(2MeBT)_2$	40.1 ± 0.6 $(26.2 \pm 0.5)^b$	500 $(520)^b$	69.0 ± 0.7	69.6
$CoBr_2(2MeBT)_2$	38.5 ± 0.4 (21.2 ± 0.9)	525 (500)	57.0 ± 0.3	57.7

Values in parenthesis refer to [a]pyridine[1,3,5] and [b]2-methylpyridine[1] analogues. [c]Tetrahedral, blue form.

TABLE 4

SPECIFIC HEAT[a] DATA FOR COMPLEXES

Complex	*a* *(cal mol^{-1})*	*b* *(cal deg^{-1} mol^{-1})*	*Experimental temp. range (K)*
$CoCl_2(BT)_2$	22.4	0.19	320–430
$CoBr_2(BT)_2$	26.5	0.20	320–450
$CoI_2(BT)_2$[b]	27.2	0.18	320–450
$MnCl_2(BT)_2$	16.0	0.23	320–400
$NiCl_2(BT)_2$	42.3	0.15	320–430
$CoCl_2(2MeBT)_2$	28.1	0.22	320–280
$CoBr_2(2MeBT)_2$	32.0	0.20	320–400

[a] $C_p = a + bT$. [b]Not suitable for ΔH of decomposition measurements.

It would also be preferable to refer the enthalpies of dissociation to the gas phase by incorporating enthalpies of sublimation of the metal halides (which are available[12]) and those of the complexes. Determination of enthalpies of sublimation of the complexes is difficult because of their low vapour pressures at room temperature and decomposition at higher temperatures. We have succeeded in determining enthalpies of sublimation of only three of the complexes over the temperature ranges indicated, as follows. $CoBr_2(BT)_2$ 29.8 ± 1.0 kcal mol^{-1} (381–399 K), $CoCl_2(2MeBT)_2$

29.3 ± 0.3 kcal mol^{-1} (332–356 K), and $CoBr_2(2MeBT)_2$ 27.5 ± 1.0 kcal mol^{-1} (335–354 K). With these data, it has been possible to calculate enthalpies of the gas-phase dissociations, $MX_2L_2(g) \rightarrow MX_2(g) + 2L(g)$, for these complexes.

These enthalpies may be equated with twice the mean bond dissociation energies of the metal–ligand bonds, $\bar{D}$, if it is assumed that the gaseous complexes are monomeric species, as seems likely. Taking the enthalpies of sublimation[12], $CoCl_2$ 54 ± 1, and $CoBr_2$ 53 ± 1 kcal mol^{-1}, we obtain the values $\bar{D}(Br_2Co\text{–}BT) = 30.8 \pm 1.2$, $\bar{D}(Cl_2Co\text{–}2MeBT) = 32.5 \pm 1$, and $\bar{D}(Pr_2Co\text{–}2MeBT) = 32.0 \pm 1.2$ kcal mol^{-1}. In all of the benzothiazole and 2-methylbenzothiazole complexes, the ligand is bonded to the metal through the nitrogen rather than the sulphur atom[6], so that these values reflect the strength of the cobalt–nitrogen bond.

Structurally, the benzothiazole and 2-methylbenzothiazole complexes are very similar to the corresponding pyridine complexes. The cobalt complexes are tetrahedral, whilst the nickel and copper complexes are octahedral (distorted in the case of copper) with halogen bridging[6]. It seems likely that the manganese and cadmium benzothiazole complexes, for which no structural data are available, will be octahedral like their pyridine analogues.

Benzothiazole is a much weaker base ($pK_a = 1.2 \pm 0.1$)[13] than pyridine ($pK_a = 5.22$)[14], so that the σ-component of the metal–nitrogen bond is expected to be weaker for benzothiazole than for pyridine as ligand. However, values of the enthalpies of decomposition $MX_2L_2(c) \rightarrow MX_2(c) + 2L(g)$, shown in Table 3, are greater, except for the single case of $NiCl_2(BT)_2$, for L = benzothiazole than for L = pyridine by between 3.5 and 11 kcal mol^{-1}. Presumably, it is enhanced π-bonding in the benzothiazole complexes which reverses the trend expected from the pK_a values. A similar situation occurs with the quinoline complexes, although the effect is less marked[1,5].

A possible explanation of the very similar ΔH values for $NiCl_2(BT)_2$ and $NiCl_2(pyridine)_2$ is that the structures of these two complexes are not the same, as is presently thought[6].

The comparatively small difference of 3.5 kcal mol^{-1} between the ΔH values for $CdCl_2(BT)_2$ and $CdCl_2(pyridine)_2$ suggests that cadmium is less able to make use of additional π-bonding than elements of the first transition series.

Methyl substitution in the 2-position of benzothiazole has no effect on the value of ΔH in the cobalt complexes, presumably because the electron releasing tendency of the methyl group, which increases the donor capacity of the nitrogen atom, offsets the steric strain which methyl substitution imposes. In the cobalt 2-methylpyridine complexes the ΔH values are considerably less than those of the corresponding pyridine complexes.

REFERENCES

1 G. Beech, C. T. Mortimer and E. G. Tyler, *J. Chem. Soc.* (*A*), (1967) 925.
2 G. Beech, S. J. Ashcroft and C. T. Mortimer, *J. Chem. Soc.* (*A*), (1967) 929.
3 G. Beech, C. T. Mortimer and E. G. Tyler, *J. Chem. Soc.* (*A*), (1967) 1111.

4 G. Beech and C. T. Mortimer, *J. Chem. Soc.* (*A*), (1967) 1115.
5 G. Beech, C. T. Mortimer and E. G. Tyler, *J. Chem. Soc.* (*A*), (1969) 512.
6 E. J. Duff, M. N. Hughes and K. J. Rutt, *J. Chem. Soc.* (*A*), (1968) 2354.
7 E. J. Duff, M. N. Hughes and K. J. Rutt, *J. Chem. Soc.* (*A*), (1969) 2101.
8 F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, Circular 500, *Nat. Bur. Stand.*, Washington, 1952.
9 D. R. Stull and G. C. Sinke, *Thermodynamic Properties of the Elements*, *Advan. Chem. Ser.*, Vol. 18, 1956.
10 M. J. O'Neill, *Anal. Chem.*, 36 (1964) 1238.
11 S. J. Ashcroft, *Thermochim. Acta*, 2 (1971) 512.
12 L. Brewer, G. R. Somayajulu and E. Brackett, *J. Amer. Chem. Soc.*, 63 (1963) 111.
13 A. Albert, R. Goldacre and J. Phillips, *J. Chem. Soc.*, (1948) 2240.
14 A. Fischer, W. J. Galloway and J. Vaughan, *J. Chem. Soc.* (*A*), (1968) 457.