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THE THERMAL DECOMPOSITION OF TRANSITION-METAL COMPLEXES CONTAINING HETEROCYCLIC LIGANDS

4. SUBSTITUTED-PYRIDINE COMPLEXES OF Mn, Ni, Cu AND Cd

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ABSTRACT

Enthalpies of the overall decomposition reactions

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

and of the intermediate stepwise loss of ligand, L, where X is Cl or Br; L is 3-chloropyridine, 3-bromopyridine, 2-chloropyridine, 2-bromopyridine, or 2-methoxypyridine; and M is Mn, Ni, Cu, or Cd have been measured by use of a differential scanning calorimeter. Enthalpies of sublimation of $NiCl_2$(3-chloropyridine)$_2$, $NiCl_2$(3-bromopyridine)$_2$ and $CuCl_2$(3-bromopyridine)$_2$ have been determined. Values of the metal–nitrogen bond dissociation energies in these compounds have been calculated. A value for the specific heat of $CuCl_2$(2-chloropyridine)$_2$ is reported.

INTRODUCTION

In the previous paper of this series[1] we reported enthalpies of thermal decomposition of the complexes MX_2L_2, where M is cobalt, X is Cl or Br, and L is 3-chloropyridine (3Clpy), 3-bromopyridine (3Brpy), 2-chloropyridine (2Clpy), 2-bromopyridine (2Brpy), or 2-methoxypyridine (2MeOpy). We now present data for the corresponding complexes in which M is manganese, nickel, copper, or cadmium.

The overall decomposition reaction (1) was divided into two stages, reactions (2) and (3), except for the cupric bromide complexes which decomposed to cuprous bromide, bromine and gaseous ligand, reaction (4).

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

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

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

$$CuBr_2L_2(c) \rightarrow CuBr(c) + \tfrac{1}{2}Br_2(g) + 2L(g) \quad (4)$$

EXPERIMENTAL

The complexes were prepared by the addition of alcoholic solutions of ligand and metal halide 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 method referred to previously[2]. The scan rate was 16 K min^{-1} in all cases 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}), and checked as before[3]. Enthalpies of sublimation were obtained by use of a DuPont thermal analyser according to Ashcroft's[4] method. Specific heat data were obtained by use of the differential scanning calorimeter according to the method described by O'Neill[5].

RESULTS

Enthalpies of the stepwise and overall decomposition reactions are shown in Tables 1 and 2, respectively. 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, and 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

ENTHALPIES OF STEPWISE DECOMPOSITION OF MX_2L_2

Complex	*Reaction*	ΔH (*kcal* mol^{-1})	T_i (*K*)	T_p (*K*)	T_f (*K*)	*Weight loss* (%)	
						obs.	*calc.*
$MnCl_2(3Clpy)_2$	(2)	16.0±0.2	440	485	500	32.9±0.3	32.17
	(3)	16.3±0.3	515	570	585		
$MnCl_2(3Brpy)_2$	(2)	15.8±0.3	435	485	500	35.9±0.6	35.76
	(3)	16.5±0.3	525	585	595		
$MnCl_2(2Clpy)_2$	(2)	15.6±0.4	455	490	510	33.0±1.0	32.17
	(3)	17.5±0.4	510	565	575		
$NiCl_2(3Clpy)_2$	(2)	15.5±0.2	465	520	530	33.3±0.2	31.82
	(3)	18.5±0.4	545	600	610		
$NiCl_2(3Brpy)_2$	(2)	15.4±0.2	495	540	560	36.9±0.4	35.46
	(3)	19.8±0.3	566	610	620		
$CuCl_2(3Clpy)_2$	(2)	16.2±0.2	435	500	510	37.8±1.8	32.41
	(3)	16.7±0.5	510	575	580		
$CuBr_2(3Clpy)_2$	(4)	42.9±0.5	450	520	535	67.9±0.6	68.15
$CuCl_2(3Brpy)_2$	(2)	16.2±0.2	450	520	530	39.0±1.1	35.07
	(3)	18.8±0.2	530	595	605		

TABLE 1 (*continued*)

Complex	*Reaction*	ΔH (*kcal mol*$^{-1}$)	T_i (*K*)	T_p (*K*)	T_f (*K*)	*Weight loss* (%)	
						obs.	*calc.*
$CuBr_2(3Brpy)_2$	(4)	40.9±1.2	465	540	560	72.5±0.1	73.40
$CuCl_2(2Clpy)_2$	(2)	14.0±0.2	370	420	430	31.6±0.2	31.39
	(3)	13.7±0.4	430	490	500		
$CuCl_2(2Brpy)_2$	(1)	25.3±0.5	335	355	365[a]		
			380	430	435		
			435	455	465		
			465	495	505	70.8±0.2	70.14
$CuBr_2(2Brpy)_2$	(4)	30.4±0.2	395	470	505	74.0±0.1	73.40
$CuCl_2(2MeOpy)_2$	(2)	14.5±0.1	370	425	435	34.1±0.2	30.94
	(3)	15.4±0.3	435	485	505		
$CdCl_2(3Clpy)_2$	(2)	14.6±0.2	425	475	485	29.1±1.5	27.61
	(3)	16.6±0.1	490	550	560		

[a] First peak corresponds to a weight loss of 2.9±0.6% and $\Delta H = 0.6 \pm 0.1$ kcal mol^{-1}, due probably to loss of solvent impurity; the following three peaks were too close to allow stoichiometry of reactions to be established.

TABLE 2

ENTHALPIES OF OVERALL DECOMPOSITION REACTION (1)
$MX_2L_2(c) \rightarrow MX_2(c) + 2L(g)$

Complex	ΔH (*kcal mol*$^{-1}$)	T_m (*K*)	*Weight loss* (%)	
			obs.	*calc.*
$MnCl_2(3Clpy)_2$	32.3±0.5	530	63.8±0.4	64.34
$MnCl_2(3Brpy)_2$	32.3±0.6	535	72.1±0.2	71.53
$MnCl_2(2Clpy)_2$	33.1±0.8	530	33.0±0.7	32.20
$NiCl_2(3Clpy)_2$	34.0±0.6	560	63.4±0.5	63.64
$NiCl_2(3Brpy)_2$	35.2±0.5	575	71.0±0.1	70.92
$CuCl_2(3Clpy)_2$	32.9±0.7	540	64.4±0.2	62.81
$CuBr_2(3Clpy)_2$	34.0±0.5[a]	540		
$CuCl_2(3Brpy)_2$	35.0±0.4	560	70.9±0.4	70.14
$CuBr_2(3Brpy)_2$	32.0±1.2[a]	540		
$CuCl_2(2Clpy)_2$	27.7±0.6	455	62.1±0.7	62.79
$CuCl_2(2Brpy)_2$	25.3±0.5	460	70.8±0.2	70.14
$CuBr_2(2Brpy)_2$	21.5±0.2[a]	470		
$CuCl_2(2MeOpy)_2$	29.9±0.4	455	62.0±0.3	61.89
$CdCl_2(3Clpy)_2$	31.2±0.3	515	55.4±0.1	55.33

[a] Calculated from $\Delta H(4)$ using the ΔH_f° values[6] $CuBr_2(c)$, −33.9 and CuBr(c), −25.0 kcal mol^{-1}.

It has been possible to determine enthalpies of sublimation of three of these complexes over the temperature ranges indicated, as follows. $NiCl_2(3Clpy)_2$ 17.2±1.7 (355–385 K), $NiCl_2(3Brpy)_2$ 18.2±1.2 (374–403 K), and $CuCl_2(3Brpy)_2$ 13.6±1.3 kcal

mol^{-1} (360–390 K). Assuming that these enthalpies are close to those at 298 K and that they refer to monomeric species in the gas phase, and taking the enthalpies of sublimation[7], $NiCl_2$ 58.7 ± 1.0 kcal mol^{-1} and $CuCl_2$ 47 ± 1 kcal mol^{-1}, we obtain the following mean bond dissociation energies: $\bar{D}(Ni–N) = 37.8 \pm 1.6$ kcal mol^{-1} in $NiCl_2(3Clpy)_2$; $\bar{D}(Ni–N) = 37.9 \pm 1.3$ kcal mol^{-1} in $NiCl_2(3Brpy)_2$; and $\bar{D}(Cu–N) = 34.2 \pm 1.3$ kcal mol^{-1} in $CuCl_2(3Brpy)_2$. Thus for the series of 3-bromopyridine complexes, $CoCl_2(3Brpy)_2$, $NiCl_2(3Brpy)_2$ and $CuCl_2(3Brpy)_2$, the values of $\bar{D}$(Metal–N) are 34.9 ± 0.8, 37.9 ± 1.3 and 34.2 ± 1.3 kcal mol^{-1}. The trend of these values is that which is expected for these metals. Further analysis of the enthalpies of the overall decomposition reaction (1), given in Table 2, must await measurement of the enthalpies of sublimation of the remaining complexes.

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