Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

THE THERMOCHEMISTRY OF SOME 2-, 3- AND 4-CYANOPYRIDINE COMPLEXES OF TRANSITION-METAL HALIDES

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(Received July 19th, 1971)

ABSTRACT

The heats of thermal decomposition of some complexes of the type ML_nX_2 ($M = Mn$, Co and Ni; $L = 2$-, 3- and 4-cyanopyridine; $X = Cl$ or Br) were measured by differential scanning calorimetry (DSC). The results indicated that the thermochemical properties of the complexes were similar to those of pyridine and dissimilar from those of benzonitrile. Comment is made upon the dependence of the heats of reaction on the nature of the metal and ligands.

INTRODUCTION

Recently, Beech *et al.* reported[1] the heats of thermal decomposition of several acetonitrile and benzonitrile complexes of transition-metal halides. For the latter, the heats of decomposition, per mole of benzonitrile, were found to be in the order $Mn > Co > Ni$. A quite different behaviour had been reoorted previously[2-4] for the analogous pyridine, and related complexes in that there was only a slight dependence of the heats of decomposition on the nature of the metal. The thermochemical behaviour of the nitrile complexes was taken to indicate[1] a progressive reduction in the importance of metal–ligand π-bonding in the Mn, Co, Ni sequence. It is possible, therefore, that π-bonding effects are much less important in the complexes of the more basic pyridine ligands which are able to form stronger σ-bonds.

There have been very few calorimetric studies of complexation by cyanopyridines and there are no previous studies of the thermal behaviour of any solid cyanopyridine complexes. Wong and Brewer[5], from their solution calorimetry studies of substituted pyridine complexation of zinc(II) chloride and copper(II) chloride, suggested that there was an appreciable π-contribution to the metal–ligand bond in complexes of 4-cyanopyridine. Earlier spectrophotometric results obtained by these workers[6] suggested that the importance of the π-contribution to the bond between 4-cyanopyridine and certain dipositive metal ions was in the order $Mn(II) > Ni(II) > Co(II)$.

The present paper constitutes an extension of the earlier results obtained for dihalogeno and diisothiocyanato[7] complexes of pyridines, substituted pyridines and benzonitrile. One object of this work was to assess the usefulness of calorimetric studies in determining the donor atom used in coordination by a ligand possessing more than one potential donor site. Cyanopyridines may coordinate via the nitrile or pyridine nitrogen atoms and infra-red studies[8] support the latter. From the difference found in the thermochemical properties of benzonitrile and pyridine complexes, discussed above, it was thought that a thermochemical study of the analogous cyanopyridine complexes might provide results which could be used to determine the mode of coordination of the ligands. It was also thought that the results could be used to determine the relative importance of σ- and π-bonding between the metals and ligands.

Ligand abbreviations used are as follows: 2-cyanopyridine (2-CP), 3-cyanopyridine (3-CP), 4-cyanopyridine (4-CP).

EXPERIMENTAL

Thermal measurements

A Perkin–Elmer differential scanning calorimeter (DSC-1B), calibrated by the heat of fusion of pure indium, was used. The experimental technique has been described earlier[2]. The calorimeter was purged continuously with dry nitrogen at 20 ml min^{-1} and all decompositions were carried out at a heating rate of 16 °K min^{-1}. Uncertainties are expressed as standard deviations of the mean.

Complexes

The preparation of many of these complexes have been described elsewhere[8].

Samples of the complexes of 2-cyanopyridine (2-CP), 3-cyanopyridine (3-CP) and 4-cyanopyridine (4-CP) were supplied by Dr. J. R. Wasson of the University of Kentucky. Satisfactory microanalyses were obtained in all cases except for Co(4-CP)$_2$Br$_2$ which retained small amounts of moisture. The complex was vacuum-dried for 5 h at 0.1 mm and a satisfactory microanalysis obtained (Found: C, 33.6; H, 2.02; N, 13.0. Calc. for Co(4-CP)$_2$Br$_2$: C, 33.6; H, 1.88; N, 13.1%). The stoicheiometries were checked by the weighed losses on thermal decomposition (see Tables I—III), except for Co(2-CP)Cl$_2$ which did not decompose to CoCl$_2$ but had a satisfactory microanalysis (Found: C, 30.8; H, 2.60; N, 11.8. Calc. for Co(2-CP)Cl$_2$: C, 30.7; H, 2.30; N, 11.9%).

RESULTS AND DISCUSSION

The complexes decomposed to the appropriate halides directly or by way of the intermediates in reactions (1)–(6):

$$ML_2X_2(\text{cryst.}) \rightarrow MLX_2(\text{cryst.}) + L(g) \qquad (1)$$
$$MLX_2(\text{cryst.}) \rightarrow MX_2(\text{cryst.}) + L(g) \qquad (2)$$
$$MLX_2(\text{cryst.}) \rightarrow ML_{1/3}X_2(\text{cryst.}) + 2/3\,L(g) \qquad (3)$$
$$ML_2X_2(\text{cryst.}) \rightarrow ML_{1/3}X_2(\text{cryst.}) + 5/3\,L(g) \qquad (4)$$
$$ML_{1/3}X_2(\text{cryst.}) \rightarrow MX_2(\text{cryst.}) + 1/3\,L(g) \qquad (5)$$
$$ML_2X_2(\text{cryst.}) \rightarrow MX_2(\text{cryst.}) + 2\,L(g) \qquad (6)$$

Also, a solid of the composition $Ni(2\text{-}CP)_{1.5}X_2$ was obtained. The heat of decomposition of this substance to $NiCl_2$(cryst.) is identified as $\Delta H(7)$ in Table III (see p. 301).

Values of $\Delta H(i)$ refer to the peak temperature, T_p, of the decomposition reaction (i) which occurred over the range T_i–T_f °K. In each case the only gaseous product was free ligand (identified by i.r. spectroscopy) and no ligand decomposition was detectable by the use of the gas-effluent analyser of the calorimeter.

Manganese complexes. — These decomposed via the intermediates $MnLCl_2$ and $MnL_{1/3}Cl_2$, although the DSC curves were not always sufficiently well-resolved to permit the accurate measurement of individual stepwise heats of decomposition. The overall heats of reaction (Table I) are in the order 3-CP > 4-CP > 2-CP and this is also the order of the T_i values. The stoicheiometries of the complexes and of their decomposition products suggest that they may possess similar structures to their pyridine analogues, which are all polymeric and octahedral[9]. In the absence of large differences in packing forces, the heats of decomposition reflect changes in Mn–N bond strengths. If the cyanopyridines each bond to the metal atom by the pyridine nitrogens then the low heat of decomposition is probably due to the low basicity of the ligand[10] and to steric hindrance by the cyano group. The fact that $\Delta H(6)$ of $Mn(3\text{-}CP)_2Cl_2$ was found to be greater than that of $Mn(4\text{-}CP)_2Cl_2$ was surprising in view of the similarity of the ligand pK_A values.

TABLE I

THERMOCHEMICAL DATA FOR 2-, 3-, AND 4-CYANOPYRIDINE COMPLEXES OF MANGANESE(II) CHLORIDE

Complex	*Reaction*	*T_i (°K)*	*T_p (°K)*	*T_f (°K)*	*ΔH (kJ mol^{-1})*	[a]*Overall weight loss (%)*	
						Observed	*Calculated*
$Mn(2\text{-}CP)_2Cl_2$	(4)	440	485	510	99±3	53.7	51.9
	(5)	535	570	580	6.0±0.5	64.3	62.3
	Overall (6)				105±3		
$Mn(3\text{-}CP)_2Cl_2$	(1)	480	510 555	570	114±1	32.1	31.1
	(5)	595	650	660	26.9±0.9	62.4	62.3
	Overall (6)				141±1		
$Mn(4\text{-}CP)_2Cl_2$	(1)	460	510	520	59±1	31.8	31.1
	(3)	530	575	590	39±2	51.9	51.9
	(5)	595	635	645	25±1	62.1	62.3
	Overall (6)				123±2		

[a] Based on initial weight of complex.

However, the 3-cyano substituent removes electron density from the 2-, 4- and

6-positions by both resonance and inductive effects. It is towards these positions that the t_{2g} electrons of the metal, being of the correct symmetry for π-bonding, would donate by a π-mechanism[11]. There may be, therefore, an enhanced π-contribution to the metal–ligand bond in this complex.

Cobalt complexes. — Each of these complexes was pale mauve and from their stoicheiometries and the positions and low intensities of the band maxima in their spectra, it was concluded that they were polymeric compounds with approximately octahedral stereochemistries about the cobalt atoms. With the exception of Co-(2-CP)Cl_2, the complexes decomposed via $CoLX_2$ and $CoL_{1/3}X_2$ to the appropriate halides, in a similar manner to the analogous pyridine complexes. Co(2-CP)Cl_2 decomposed to charred, unidentified products. It is possible that, in this complex, both the nitrile and pyridine nitrogens are involved in coordination to produce a thermally stable cross-linked structure. The action of heat would then be expected to cause ligand fragmentation rather than ligand removal as was observed to occur with the cross-linked cobalt complexes of 1,2- and 1,3-diazines and of 1,3,5-triazine[12].

For both the chloride and the bromide the heats of decomposition of the 3- and 4-cyanopyridine complexes were found (Table II), to be similar. This suggests that

TABLE II

THERMOCHEMICAL DATA FOR 3- AND 4-CYANOPYRIDINE COMPLEXES OF COBALT(II) HALIDES

Complex	*Reaction*	T_i (°K)	T_p (°K)	T_f (°K)	ΔH (kJ mol^{-1})	*Overall weight loss* (%)	
						Observed	*Calculated*
$Co(3\text{-}CP)_2Cl_2$	(1)	470	520	525	75±2	30.7	30.8
	(3)	535	560	570	46.6±0.9	51.9	51.3
	(5)	585	610	630	25.6±0.4	61.1	61.6
	Overall (6)				147±2		
$Co(4\text{-}CP)_2Cl_2$	(1)	440	500	510	62.1±0.8	30.8	30.8
	(3)	540	590	600	58±2	51.9	51.3
	(5)	610	650	670	30.2±0.9	61.4	61.6
	Overall (6)				150±2		
$Co(3\text{-}CP)_2Br_2$	(1)	440	515	520	66.7±0.3	24.3	24.4
	(2)	525	590	600	90±1	48.6	48.8
	Overall (6)				157±1		
$Co(4\text{-}CP)_2Br_2$	(1)	440	510	520	66.8±0.4	24.9	24.4
	(2)	540	610 630	650	94.9±0.6	49.4	48.8
	Overall (6)				161.7±0.7		

π-bonding effects are of less importance for the cobalt complexes. The lack of dependence of $\Delta H(6)$ on the nature of the halogen has been observed previously and is yet another similarity between the pyridine and cyanopyridine complexes.

Nickel complexes. — A 2-cyanopyridine complex of nickel was obtained with difficulty and analysed for the stoicheiometry, $Ni(2\text{-}CP)_{1.5}Cl_2$. The substance probably consisted of a mixture of $Ni(2\text{-}CP)_2Cl_2$ and $Ni(2\text{-}CP)Cl_2$. Since $\Delta H(1) \approx \Delta H(2)$ for most of the complexes studied (Table III), it was thought that no significant error would be introduced by the approximation, $\Delta H(6) \approx \frac{4}{3} \times \Delta H(7)$. Each of the other complexes decomposed via $NiLCl_2$ to $NiCl_2$. The $\Delta H(6)$ values are in the order 4-CP ≈ 3-CP > 2-CP and this reflects the order of ligand basicities as judged by their pK_A values[1c]. The structures of several cyanopyridine complexes of nickel halides are octahedral and polymeric and i.r. spectra indicate that coordination takes place to the nickel atom from the pyridine nitrogen. The low $\Delta H(6)$ of $Ni(2\text{-}CP)_2Cl_2$ may, therefore, again reflect a steric interaction as suggested for the manganese complex.

TABLE III

THERMOCHEMICAL DATA FOR 2-, 3-, AND 4-CYANOPYRIDINE COMPLEXES OF NICKEL(II) CHLORIDE

Complex	*Reaction*	T_i (°K)	T_p (°K)	T_f (°K)	ΔH ($kJ\ mol^{-1}$)	*Overall weight loss(%)*	
						Observed	*Calculated*
$Ni(2\text{-}CP)_{1.5}Cl_2$	(7)	460	525	555	78±1	53.2	51.3
	(6)[a]				104		
$Ni(3\text{-}CP)_2Cl_2$	(6)	490	565 590	620	152±2	61.9	61.6
$Ni(4\text{-}CP)_2Cl_2$	(1)	470	520	530	62.6±0.9	30.8	30.8
	(2)	590	640	650	88±3	61.7	61.6
	Overall (6)				151±3		

[a] Corrected from (7), see text (p. 299).

Since the complexes decomposed on heating, it was not possible to measure their heats of sublimation. Heat capacity data for the gaseous complexes and ligands are also not available, thus precluding the calculation of gas-phase enthalpy changes. However, the metal halides have quite similar heats of sublimation[13] and since the complexes, and their decomposition products probably possess similar polymeric structures it was presumed that the gaseous enthalpy would be in a similar order to those reported here. The latter, then, probably reflect differences in metal–ligand bond strengths.

If this is so, then it would appear from the arguments presented above that the results are best explained by the assumption of coordination by the pyridine nitrogen. Not only were the magnitudes of the heats of decomposition similar to those of the pyridine complexes but, also, their dependence on the central atom was identical: $Ni \approx Co < Mn$. Coordination from the pyridine nitrogen is in agreement with the spectroscopic results of Walton[8] and with the exploratory quantum-mechanical studies of Wasson[14]. The results of the latter indicated that 3- and 4-cyanopyridine should coordinate by the nitrogen atoms but that 2-cyanopyridine could coordinate by either the pyridine- or the nitrile-nitrogen. Changes in the i.r. stretching frequencies of the nitrile groups in $Mn(2\text{-}CP)_2Cl_2$ and $Ni(2\text{-}CP)_{1.5}Cl_2$ are small and of little diagnostic value.

This work has confirmed the weakness of π-bonding to cobalt(II), as suggested by Wong and Brewer[6] and has shown that π-bonding effects are greatest for Mn(II). It is probable that some degree of π-bonding exists in each of the complexes studied to strengthen the σ-bonds from these weakly basic ligands.

ACKNOWLEDGMENTS

I thank Dr. J. R. Wasson for providing samples of the cyanopyridine complexes and for making available certain Hückel electron-density studies prior to publication.

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