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The effect of KI on the thermal decomposition of cobalt(III)–ammine complexes

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Abstract

Evolved gas analysis (EGA) was used to investigate the effect of KI on the thermal decomposition of five cobalt(III)–ammine complexes, $[Co(NH_3)_5N_3]Cl_2$, $[Co(NH_3)_5NO_2]Cl_2$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_4CO_3]Cl$ and $[Co(NH_3)_6]Cl_3$, in a hydrogen atmosphere. It was found that the presence of KI shifts the thermal decomposition of these complexes to a lower temperature, and decreases the activation energies of the deammination reactions. The electron transfer from I^- to Co(III) is believed to play an important role in the decomposition process.

INTRODUCTION

Solid state chemistry is of fundamental importance in material science. Much research has focussed on the behaviour of inorganic oxides at elevated temperatures. However, there have been few studies on the behaviour of coordination compounds at low temperatures of heating.

It is well known that most solid state studies of coordination compounds have considered the thermal decompositions of single component systems [1]. The effects of added salts on the decomposition reactions remain unclear, except for the reaction of $[Co(en)_3]Cl_3$ with NH_4Y (where Y is F, Cl, Br, I) investigated by Wendlandt and Sveum [2].

We have explored the reactions of $[Co(NH_3)_6]Cl_3$ with some inorganic anion salts in the solid state [3]. The results showed that the thermal stability of $[Co(NH_3)_6]Cl_3$ decreased significantly in the presence of KSCN and KI. The effect of KSCN on the decomposition of cobalt(III)–ammine complexes has been studied recently [4]. To define further the role of KI in such reactions, five cobalt(III)–ammine complexes are investigated here, using $[Ni(NH_3)_6]Cl_2$ as a comparison. It is suggested that the redox properties of both the pure complexes and of those with added KI, affect appreciably their thermal stabilities.

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EXPERIMENTAL

Materials

The KI used was Analar grade. The $[Co(NH_3)_5N_3]Cl_2$ [5], $[Co(NH_3)_5NO_2]Cl_2$ [6], $[Co(NH_3)_5Cl]Cl_2$ [7], $[Co(NH_3)_4CO_3]Cl$ [8] and $[Co(NH_3)_6]Cl_3$ [9] complexes were prepared according to the literature methods.

Samples were obtained by mixing the complex with KI in 1:4 molar ratio and grinding in a mortar.

Apparatus

The apparatus used was constructed in this laboratory. The conditions were similar to those described previously [4, 10]. The various gas chromatographic patterns for the evolved gases could be obtained as a function of temperature. The X-ray diffractograms were obtained using a Shimadzu model XD-3A X-ray diffractometer with a copper target.

Kinetic parameters

The kinetic parameters were determined from the kinetic relationship

$$g(\alpha) = \int_{T_1}^{T_2} k_0 \exp\left(-\frac{E}{RT}\right) \mathrm{d}T$$

The equation was solved by the widely employed approximation of Coats and Redfern [11], to give the expression

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT}$$

where α is the fraction decomposed, with A being the frequency factor, β the heating rate and E the activation energy. The expression $g(\alpha)$ depends on the physical mechanism of the solid state reaction as reported in the literature [12].

RESULTS AND DISCUSSION

Figure 1 gives the EGA curves of the cobalt(III)–ammine complexes, both pure and with added KI, in the range 40–400°C in a hydrogen atmosphere. It is evident that the stabilities of all the complexes decrease in the presence of KI.

Taking $[Co(NH_3)_5Cl]Cl_2$ as an example, the evolution of ammonia from the pure complex begins at about 180°C; the maximum intensity for gas evolution is at 280°C, followed by a second broad peak at 340°C (see Fig. 1c), which is in agreement with the results reported by Watt [13] for a

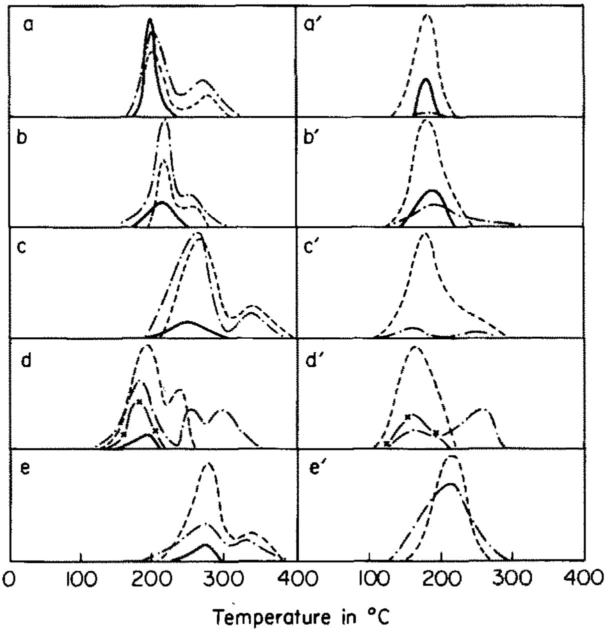

Fig. 1. EGA curves of cobalt(III)–ammine systems in a hydrogen atmosphere: a, $[Co(NH_3)_5N_3]Cl_2$; a′, $[Co(NH_3)_5N_3]Cl_2 + KI$; b, $[Co(NH_3)_5NO_2]Cl_2$; b′, $[Co(NH_3)_5NO_2]Cl_2 + KI$; c, $[Co(NH_3)_5Cl]Cl_2$; c′, $[Co(NH_3)_5Cl]Cl_2 + KI$; d, $[Co(NH_3)_4CO_3]Cl$; d′, $[Co(NH_3)_4CO_3]Cl + KI$; e, $[Co(NH_3)_6]Cl_3$; e′, $[Co(NH_3)_6]Cl_3 + KI$. ---, NH_3; — —, N_2; – × –, Co_2; – · –, HCl (a, c, e), H_2O (b), $H_2O + HCl$ (d), HCl + HI (a′, c′, e′), $H_2O + HI$ (b′, d′).

nitrogen atmosphere. The stoichiometry of the thermal decomposition of $[Co(NH_3)_5Cl]Cl_2$ agrees with that previously proposed by Wendlandt and Smith [14] and Watt [13] as:

$$6[Co(NH_3)_5Cl]Cl_2 \rightarrow 6CoCl_2 + N_2 + 6NH_4Cl + 22NH_3$$

In the presence of KI, the evolution of ammonia starts at about 100°C; the corresponding peak temperature is 180°C (Table 1), which is 100°C

TABLE 1

The peak temperature of solid state deammination reactions in a hydrogen atmosphere

Sample	Peak temperature/°C	Sample	Peak temperature/°C
$[Co(NH_3)_5N_3]Cl_2$	210	$[Co(NH_3)_5N_3]Cl_2 + KI$	180
$[Co(NH_3)_5NO_2]Cl_2$	220	$[Co(NH_3)_5NO_2]Cl_2 + KI$	180
$[Co(NH_3)_5Cl]Cl_2$	280	$[Co(NH_3)_5Cl]Cl_2 + KI$	180
$[Co(NH_3)_6]Cl_3$	290	$[Co(NH_3)_6]Cl_3 + KI$	220
$[Ni(NH_3)_6]Cl_2$	160	$[Ni(NH_3)_6]Cl_2 + KI$	160

TABLE 2

Activation energy of solid state deammination reactions in a hydrogen atmosphere

Sample	Mechanism	E_a/ kJ mol^{-1}	Sample	Mechanism	E_a/ kJ mol^{-1}
$[Co(NH_3)_5N_3]Cl_2$	F_1	170	$[Co(NH_3)_5N_3]Cl_2 + KI$	F_1	118
$[Co(NH_3)_5NO_2]Cl_2$	F_1	148	$[Co(NH_3)_5NO_2]Cl_2 + KI$	F_1	73
$[Co(NH_3)_5Cl]Cl_2$	F_1	107	$[Co(NH_3)_5Cl]Cl_2 + KI$	F_1	94
$[Co(NH_3)_6]Cl_3$	F_1	129	$[Co(NH_3)_6]Cl_3 + KI$	F_1	90
$[Ni(NH_3)_6]Cl_2$	F_1	103	$[Ni(NH_3)_6]Cl_2 + KI$	F_1	109

lower than that of the pure complex, with no N_2 appearing on the EGA curve. The deammination activation energy also changes from 107 to 94 kJ mol^{-1}. XRD demonstrated presence of KCl and $CoCl_2$, together with excess KI, in the solid product. This process is suggested to take place as follows:

$$2[Co(NH_3)_5Cl]Cl_2 + 2KI \rightarrow 2CoCl_2 + 10NH_3 + I_2 + 2KCl$$

$$I_2 + H_2 \rightarrow 2HI$$

For the other cobalt(III)–ammine complexes, $[Co(NH_3)_5N_3]Cl_2$, $[Co(NH_3)_5NO_2]Cl_2$, $[CoNH_3)_4Co_3]Cl$ or $[Co(NH_3)_6]Cl_3$, an analogous process occurs, with the peak temperature and deammination activation energy decreasing to different degrees as shown in Tables 1 and 2, and with no N_2 appearing for the $[Co(NH_3)_4CO_3]Cl$–KI and $[Co(NH_3)_6]Cl_3$–KI systems (Fig. 1). For the $[Co(NH_3)_5N_3]Cl_2$–KI and $[Co(NH_3)_5NO_2]Cl_2$–KI systems, N_2 is also detected; this could be interpreted as a result of the N_3^- and NO_2^- ions participating in the redox process.

In addition, Fig. 1 shows that the thermal decomposition of the pure complexes proceeds in two steps. For those with added KI only one ammonia peak is noted which confirms that the attachment of excess I^- accelerates the decomposition to only one step. Similar results have been obtained for systems with added Cl^- and Br^- [3].

In the thermal decomposition process of Co(III)–ammine complexes, the formation of a transient state $[Co^{III}–NH_2^{\delta-} \cdots H^{\delta+}]$ is induced [15]. The dissociation of this transient species to H^+ and NH_2 can be accelerated by a concomitant electron transfer from the NH_2^- moiety to the cobalt(III) and by a subsequent nitrogen-forming reaction [15]. For the complexes containing iodide, as Simmons and Wendlandt [16] proposed, the reducing agent could be coordinated ammonia, coordinated iodide ion or ionic iodide ion. In the present work, with excess KI ($E^{\ominus}_{I_2/I^-} = 0.535$ V) present, such electron transfer ($I^- \rightarrow Co(III)$) becomes much easier and thus makes the complexes decompose at a lower temperature.

With $[Ni(NH_3)_6]Cl_2$, there is no electron transfer observed during the

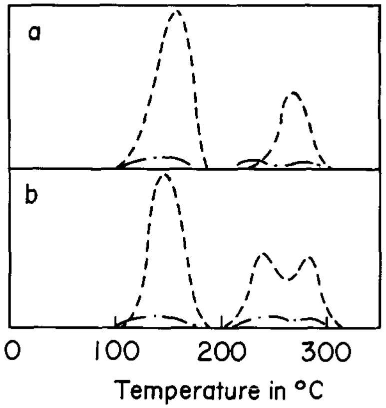

Fig. 2. EGA curves of $[Ni(NH_3)_6]Cl_2$ in a hydrogen atmosphere: a, $[Ni(NH_3)_6]Cl_2$; b, $[Ni(NH_3)_6]Cl_2 + KI$. ----, NH_3; – · –, HCl (a), HCl + HI (b).

decomposition process, and the first peak temperature (Fig. 2, Table 1) and the corresponding deammination activation energy (Table 2) remain almost unchanged in the presence of KI. The difference in the second peak may reflect the iodide ion's participation in intermediate formation. Thus, the redox properties of both the pure complex and with added I^- affect the thermal stabilities of the cobalt(III)–ammine complexes.

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