October, 1984] © *1984 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 57, 3005—3006 (1984)* 3005

Thermal Decomposition of Cobalt(II) Halide Complexes of Tetramethylurea and Related Cyclic Ureas

Kozo Sone,* Masae Kikuchi,† Kaede Ogasawara, Miuaco Kawashita Kuya,†† and Anamaria Dias Pereira††
Department of Chemistry, Faculty of Science, Ochanomizu University, Otsuka 2-1-1, Bunkyo-ku, Tokyo 112
†*Institute for Iron, Steel and Other Metals, Tohoku University, Katahira-cho, Sendai 980*
††*Instituto de Química, Universidade de São Paulo, Cidade Universitária, C.P.20.780, São Paulo, Brazil*

(Received May 1, 1984)

Synopsis. TG-DTA studies revealed that the complexes CoX_2L_2 (L=tmu, dmeu or dmpu (see text); X=Cl, Br or I) decompose into CoX_2 and 2L by slight heating. The ease of this decomposition decreases in the orders of tmu>dmeu>dmpu and Cl>Br>I, corresponding to the orders of coordination abilities of these ligands.

In connection with the recent studies of Kuya *et al.* on the cobalt (II) halide complexes of dimethyl ethyleneurea (dmeu) and dimethyl trimethyleneurea (dmpu),[1,**)] we carried out a comparative study on the thermal behaviors of these complexes and also those of the corresponding complexes of tetramethylurea (tmu), reported formerly by King.[2)] All these complexes are of the general formula CoX_2L_2 (L= tmu, dmeu or dmpu; X=Cl, Br or I), and their spectral, magnetic and conductometric studies indicated that they are composed of tetrahedral, high-spin and uncharged species, *i.e.*, $[CoX_2L_2]$, in which the L molecules are coordinated to Co (II) at their C=O groups.[1,2)]

Experimental

Preparation of the Complexes. The complexes of dmpu, and the Cl- and Br-complexes of dmeu, were prepared as reported elsewhere.[1)] The remaining complexes were prepared by stirring anhydrous CoX_2 with 1,2-dichloroethane, in which it is nearly insoluble, and dropping L into the mixture, until complete dissolution of CoX_2 took place. The blue or bluish green solution formed was then evaporated under vacuum, until large crystals of the same color separated out. The purity of the crystals was confirmed by elementary analysis, and also by the TG data (especially Δw in vacuum; *cf.* Table 1).

TG–DTA Measurements. The thermogravimetric (TG) and differential thermal analysis (DTA) measurements were carried out with a Sinku-Riko TGD-3000 Differential Thermobalance, in static air, in flowing N_2 (flow rate: 50 cm^{3}min^{-1}) and in vacuum (3 Torr; 1 Torr=133 N m^{-2}). 15—20 mg of the sample was taken for each run, and heated at a rate of 4 °C min^{-1}.

Results and Discussion

Figure 1 shows the TG curves of the dmpu complexes, and the DTA curve of $[CoBr_2(dmpu)_2]$, both measured in flowing N_2. The TG and DTA curves of the remaining complexes are essentially similar to these. All the TG curves show a wide decomposition step, and the weight loss for it agrees, in each case, reasonably well with the stoichiometry of the following decomposition (1):

$$[CoX_2L_2] \longrightarrow CoX_2 + 2L, \qquad (1)$$

in which all the organic ligands are driven off in the gas phase, leaving cobalt halides behind. On the other hand, the DTA curves are composed of a sharp endothermic peak appearing at 90—150 °C, and another endothermic peak near the end of the decomposition step on the TG curve. Visual observation confirmed that the former corresponds to the melting point; the fact that it is so low indicates that these complexes are essentially molecular crystals, supporting their formulation.[1,2)] The latter corresponds apparently to the absorption of heat of the decomposition, together with the heat of vaporization of evolved L. In certain cases, another very weakly endothermic peak appears before melting (mostly at 70—80 °C), which may be due to some phase transition in the solid.

Comparing all these data, which are also summarized in Table 1, we can readily recognize that the ease of the reaction (1) in N_2 decreases in the following orders of L and X:

L: tmu>dmeu>dmpu
X: Cl>Br>I

The meaning of these orders can be explained as follows. In the course of the decomposition (1), the ligands L are driven out of the coordination sphere, but the driving force for it must be the attack by the anions X^- belonging to the surrounding complexes, which tend to form Co-X-Co bridges leading, eventually, to the formation of the layer lattice structure of CoX_2. In other words, we can say that the ligands L are squeezed out of the coordination sphere by the anions X^-. The ease of the decomposition will then increase with the

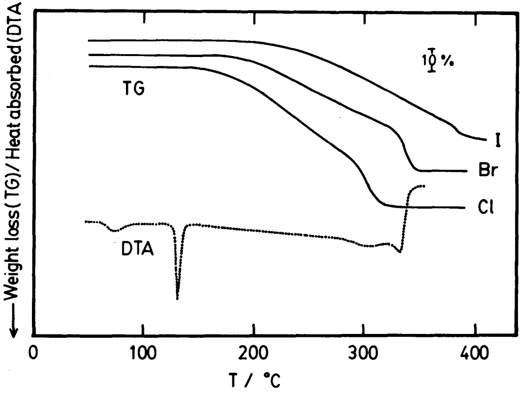

Fig. 1. TG curves of the dmpu complexes, and DTA curve of $[CoBr_2(dmpu)_2]$, in flowing N_2.

[**)] According to the IUPAC nomenclature, dmeu and dmpu are 1,3-dimethyl-2-imidazolidinone and 1,3-dimethylhexahydro-2-pyrimidinone, respectively.

Table 1. TC–DTA data of the complexes: temperature ranges and weight losses(Δw) for the decomposition step, and DTA peak positions

Complex	In N_2			In vacuum		Δw/%
	Temp range/°C	Δw/%	DTA peaks[a)]/°C	Temp range/°C	Δw/%	(Calcd)[b)]
$[CoCl_2(tmu)_2]$	80—260	61.4	*91*, 239	50—205	64.7	64.1
$[CoBr_2(tmu)_2]$	100—300	48.5	*97*, 289	65—180	49.2	51.5
$[CoI_2(tmu)_2]$	120—380	46.6	*131*, —[c)]	85—245	41.3	42.6
$[CoCl_2(dmeu)_2]$	125—350	60.0	(76), *127*, 252	70—220	62.0	63.7
$[CoBr_2(dmeu)_2]$	125—310	49.4	(72), *138*, 290	85—255	48.9	51.1
$[CoI_2(dmeu)_2]$	110[d)]—430	43.0	*134*, —[c)]	70—245	41.4	42.2
$[CoCl_2(dmpu)_2]$	120—340	64.9	(101), *127*, 313	85—220	65.2	66.4
$[CoBr_2(dmpu)_2]$	150—365	52.8	(70), *130*, 344	100—260	53.0	54.0
$[CoI_2(dmpu)_2]$	170—410	45.2	*146*, 384	115—250	43.6	45.0

a) The peaks for melting points are italicized, and those for solid phase transitions are in parentheses. b) Calculated according to the eq.(1). c) Scarcely perceptible. d) Sizable decomposition begins at *ca.*160 °C.

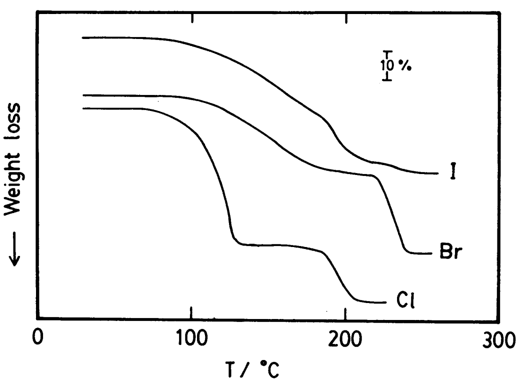

Fig. 2. TG curves of the dmeu complexes in vacuum.

increase of the coordination ability of X^-, *i.e.*, in the direction of $I^- \rightarrow Br^- \rightarrow Cl^-$, and also with the decrease of the coordination ability of L. As one can easily see from their dipole moments (tmu: 3.49D, dmeu: 4.09D, dmpu: 4.23D; solvent: dioxane, $1\,D = 3.33 \times 10^{-30}\,Cm$), the latter ability will be the lowest with tmu, and will increase through dmeu to dmpu.[3,4]

Similar measurements were also made in static air and in vacuum. The data in air was found to be essentially similar to those in N_2, but those in vacuum were notably different. As can be seen from Table 1, the temperature range for the decomposition is notably lowered by evacuation, and, although the general appearance of the TG curves indicate that the two orders of L and X still approximately hold, small shoulders indicating stepwise release of L are observed on most of them. The most significant ones are those of $[CoX_2(dmeu)_2]$ shown in Fig. 2, which reveal that Cl- and Br-complexes of definite intermediate compositions, *i.e.*,$CoCl_2(dmeu)_{2/3}$ and $CoBr_2(dmeu)$, are formed in the course of the decomposition (1). Intermediate complexes of similar stoichiometries, with probably polymeric structures, have been observed in the thermal decompositions of other CoX_2L_2-type complexes.[5,6] The DTA curves in vacuum are rather complicated, with several endothermic peaks corresponding to the successive steps.

We can thus conclude that this decomposition can be understood as the competition of the coordination tendencies of the leaving and entering groups, as is commonly encountered among the ligand exchange reactions.[7,8]

References

1) M. K. Kuya, A. D. Pereira, E. Giesbrecht, and K. Sone, *Anais Acad. Brasil. Ciênc.*, **56**, 147 (1984).

2) T. M. King, Ph. D. Thesis, Univ. of Tennessee (1966).

3) A. L. McClellan, "Tables of Experimental Dipole Moments," Freeman, San Francisco (1963), p. 153.

4) E. J. Lien and W. D. Kumler, *J. Med. Chem.*, **11**, 214 (1968).

5) J. R. Allan, D. H. Brown, R. H. Nuttall, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **26**, 1895 (1964).

6) D. H. Brown, R. H. Nuttall, and D. W. A. Sharp, *ibid.*, **26**, 1151 (1964).

7) As to a related TG-DTA study on the tmu complexes of lanthanoids, *cf.* K. Sone, K. Nagase, M. K. Kuya, and E. Giesbrecht, *Bull. Chem. Soc. Jpn.*, **55**,449 (1982).

8) It may be added that the fully alkylated ureas studied here are all liquids which boil near or above 200 °C, and are thermally very stable. Further decomposition of the released ligand will thus be quite unlikely, at least for the most part of the decomposition step.