Journal of Thermal Analysis, Vol. 6 (1974) 299—304

THERMAL DECOMPOSITION OF POTASSIUM SALTS OF CYANO-HALOGENO COMPLEXES OF MERCURY(II)

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(Received October 23, 1972)

The thermal decompositions of $Hg(CN)_2$, $K_2Hg(CN)_4$, $KHg(CN)_2Cl \cdot H_2O$ $KHg(CN)_2Br$ and $KHg(CN)_2I$ were studied. The results showed that each of the studied complexes decomposes at a lower temperature than $Hg(CN)_2$ itself. The halogen-containing complexes decompose in two ways. In $KHg(CN)_2Cl \cdot H_2O$ the Hg—CN bond is first broken, and then Hg_2Cl_2, $(CN)_2$ and KCN are formed. The first step in the decomposition of $KHg(CN)_2Br$ and $KHg(CN)_2I$, on the other hand, is the decomposition to $Hg(CN)_2$ and KBr or KI.

Mercury(II) cyanide forms numerous addition compounds with various salts and coordinatively saturated, inert transition metal cyano complexes [1]. Our earlier studies have shown that these latter also react with mercury(II) cyanide in aqueous solution [2]. With the primary aim of investigating the heteropolynuclear complexes thus formed, a study has been made of the thermal decomposition of a number of solid adducts, among them compounds formed with potassium halides. The present paper gives an account of the results obtained with this latter group.

Experimental

The following compounds were used for derivatographic studies: $Hg(CN)_2$ (Mallinckrodt DAB 6, A. R.), $K_2Hg(CN)_4$ (Riedel, A. R.), $KHg(CN)_2Cl \cdot H_2O$, $KHg(CN)_2Br$ and $KHg(CN)_2I$. These last three compounds were prepared by the following method. A boiling, concentrated aqueous solution of $Hg(CN)_2$ was mixed with a boiling, concentrated aqueous solution of potassium halide, containing a greater amount than the equivalent. On cooling the mixed complex crystallized out. The crystals were filtered, washed with alcohol, and dried in the air.

The thermal studies were made with a MOM G—425 Derivatograph, in a corundum crucible, with α-Al_2O_3 as inert substance and argon as inert gas. Other operating conditions: T_{max}: 600, 900°; heating rate: 10°/min; TG sensitivity: 200 (500) mg; DTG sensitivity: 1/15; DTA sensitivity: 1/10.

The weight of sample was 200—500 mg (0.5—1.5 mmol). The weight losses observed on the TG curves were referred to 1 mole of complex. In this way the amount of material released during the decomposition could be compared directly with the molecular weight. (This is more advantageous in the identification of the decomposition product than the normal weight loss given as a percentage.) In the cases when the amount of material released was found to be stoichiometric, the number of moles of the decomposition product and its identity (e.g. 1/2 Hg_2Cl_2) were noted along the TG curves.

Results and discussion

1. The thermal curves of $Hg(CN)_2$ are given in Fig. 1a. At the beginning the compound loses weight continuously. From about 350° on the decomposition accelerates, the rate reaching 450°. This is associated with a strong, broad endothermic DTA peak; the broadness can be explained in that the decomposition of $Hg(CN)_2$ and the evaporation of the metallic mercury formed proceed simultaneously. The total weight decrease is somewhat less than the value corresponding to 1 mole Hg + 1 mole $(CN)_2$. The reason for this is that at the end of the decomposition a small amount of carbon remains.

2. The thermal curves of $K_2Hg(CN)_4$ can be seen in Fig. 1b. The weight of this compound is constant up to about 400°, but from then on it decomposes increasingly rapidly. The maximum rate is attained at 435°. The decomposition is accompained by a strong, broad endothermic effect. The weight loss corresponds to ~ 1 mole Hg and ~ 1 mole $(CN)_2$. It can be seen that $K_2Hg(CN)_4$ decomposes in a much narrower temperature range than $Hg(CN)_2$, as a consequence of the regulating effect of the additional KCN.

The final stages on the TG curve correspond to the melting (580°) and decomposition of KCN, and to the evaporation of the cyanogen and metallic potassium formed (above 750°).

In another experiment the compound was heated only to 580°, and then cooled. On renewed heating the material obtained melted at 640°, the literature [3] m. p. of KCN. These data indicate that the KCN with a m.p. of 580° remaining after the loss of the $Hg(CN)_2$ from the $K_2Hg(CN)_4$ is an unstable modification; its loosened crystal lattice remaining from the original complex is not the same as the lattice of KCN with a m.p. of 640° which is stable under normal conditions.

Because of a small residue of carbon in the crucible the weight loss is somewhat less than the theoretical, here, too.

3. Fig. 1c shows the thermal curves of $KHg(CN)_2Cl \cdot H_2O$. In the first step 1 mole of water is split off, the peak temperature being 120°. A protracted stage then follows in the temperature range 130–310° (second step); this is associated with a very flat, broad endothermic DTA peak. Since the weight loss corresponds to exactly 0.5 mole $(CN)_2$, and the section of the TG curve above 500° agrees with the same section of the curve for $K_2Hg(CN)_4$, it was assumed that the following intramolecular reaction occurs in this stage of the decomposition:

$$KHg(CN)_2Cl \rightarrow 1/2\,(CN)_2 + 1/2\,Hg_2Cl_2 + KCN \qquad (1)$$

The occurrence of this process is confirmed by the following experimental facts:

a) The total height of the third step (330–630°) corresponds exactly to the loss of 0.5 mole Hg_2Cl_2.

b) The temperature peaks at 330 and 380° can be identified with the melting and boiling points of Hg_2Cl_2 (m.p.: 302°; b.p.: 383.7° [4]). On the DTG and DTA curves it is possible to observe two processes with different rates and thermal effects; the second of these is the faster (the turning point is marked

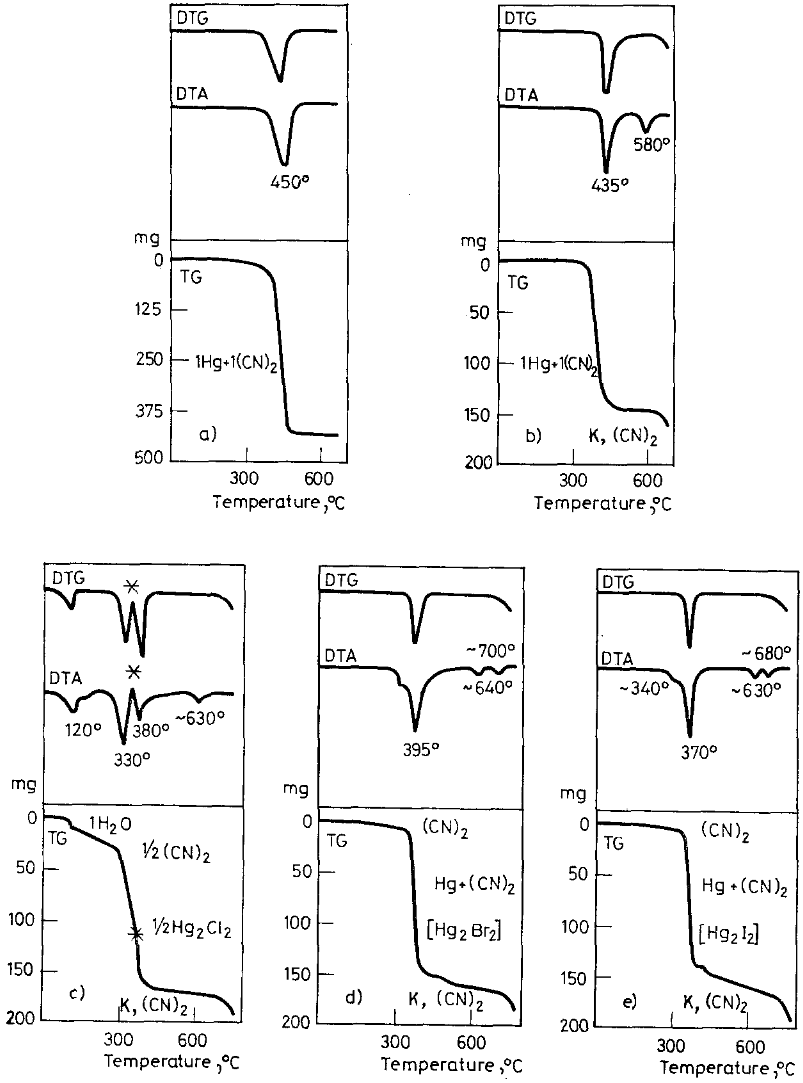

Fig. 1. TG, DTG and DTA curves of the complexes a) $Hg(CN)_2$; b) $K_2Hg\ (CN)_4$ and c), d), e) $KHg(CN)_2X$ (X: Cl, Br, I)

by *). After the melting point, and then the boiling point, are reached, therefore the Hg_2Cl_2 is lost at an increasing rate.

c) The assumed reaction (1) is also supported by analytical data. In an apparatus which could be heated stage-wise, on samples heated up to 300° and to 450°, 0.44–0.47 mole and 0.53 mole cyanogen, respectively, calculated for 1 mole complex, could be determined. This means that during the third step, the loss of Hg_2Cl_2, there is practically no further formation of cyanogen. Hence the formation of Hg_2Cl_2 is virtually complete.

d) A white powder, together with a smaller amount of grey material, is deposited on the cooler parts of this same apparatus. On the action of ammonia the white powder turns black, indicating the presence of Hg_2Cl_2. Naturally, the starting compound does not give this reaction.

e) The form of the last section of the TG curve is similar to the corresponding section on the curve for $K_2Hg(CN)_4$. The weak endothermic effect at about 630° corresponds to the melting of KCN (m.p.: 601–621°; or 634.5° [3]). After this the KCN gradually decomposes and from 780° evaporates at a rate corresponding to the formation of metallic potassium (b.p.: 776° [4]).

4. The thermal curves of $KHg(CN)_2Br$ are shown in Fig. 1d. A little cyanogen is formed in the first "step". 0.17 mole $(CN)_2$ was formed per mole from a sample heated to 300° in a stage-heated furnace, and the greyish deposit observed on the cooler parts was further darkened on the action of ammonia. From a comparison of these observations with what was said in connection with the thermal decomposition of $KHg(CN)_2Cl \cdot H_2O$, it can be stated that in the case of the bromide complex the Hg(II) → Hg(I) reduction is only partial, and the following two parallel reactions must be considered:

$$KHg(CN)_2Br \rightarrow Hg(CN)_2 + KBr \tag{2}$$

$$KHg(CN)_2Br \rightarrow 1/2\, Hg_2Br_2 + 1/2\, (CN)_2 + KCN \tag{3}$$

This can primarily be deduced from the DTG and DTA curves of the compounds, which exhibit a single strong, broad, endothermic peak. The weight decrease observed on the TG curve corresponds to the joint loss of ~ 1 mole Hg + ~ 1 mole $(CN)_2$ and a little Hg_2Br_2. This step therefore involves principally the decomposition of $Hg(CN)_2$ with a peak temperature of 395°.

The weak endothermic effects on the DTA curve at ~ 350°, ~640° and ~700° can be identified with the temperature of sublimation of Hg_2Br_2 (T_{subl}: 345° [4]), and the melting points of KCN and KBr (m.p.: 730° [3]).

The last section of the curve is essentially the same as the corresponding section of the curves of the two preceding compounds.

5. The thermal curves of the complex $KHg(CN)_2I$ are to be seen in Fig. 1e. The thermal curves show that the decomposition of $KHg(CN)_2I$ is similar to that of $KHg(CN)_2Br$. Here too the first step is small, indicating a decomposition analogous to Eq. (3). The second step is the decomposition of $Hg(CN)_2$, with a peak temperature of 370°. The other endothermic effects on

the DTA curve are only weak, since Hg_2I_2 and KCN are scarcely formed (Hg_2I_2 m.p.: 290 °C; b.p.: 310° [3, 4]; KI m.p.: 681.8° [4]).

The presence of Hg_2I_2 and the formation of a small amount ($\sim$0.22 mole) of cyanogen were confirmed similarly as above.

The thermal curves show that the decomposition of the lattice of each of the complexes studied takes place at a lower temperature than the decomposition of $Hg(CN)_2$ itself. This means that the $Hg(CN)_2$ can be split out from the lattices of the complexes more easily than from its own lattice. The temperatures of decomposition of the compounds studied are:

$Hg(CN)_2$	$K_2Hg(CN)_4$	$KHg(CN)_2Cl$	$KHg(CN)_2Br$	$KHg(CN)_2I$
450°	435°	(330°)	395°	370°

(In the case of the decomposition of $KHg(CN)_2Cl \cdot H_2O$, Hg_2Cl_2 is lost.)

It is worthy to note that the temperatures of decomposition of the halide complexes do not show a unidirectional change as the halogen atom is varied. The reason for this is that the nature of the decomposition of the chloro complex is different from those of the other complexes.

The thermal curves and the supplementary analytical examinations showed that the complexes of the type $KHg(CN)_2X \cdot yH_2O$ decompose in two ways on the action of heat. After the loss of the water of crystallization, in one type the Hg–CN bonds are first broken and Hg_2X_2, $(CN)_2$ and KCN are formed. On further heating these decompose or are released. In the other case $Hg(CN)_2$ and KX are first formed, which decompose or are lost on further heating.

The thermal decomposition of $KHg(CN)_2Cl \cdot H_2O$ proceeds almost quantitatively according to the first type. This was clearly confirmed by the evaluation of the TG, DTA and DTG curves, and by the analytical detection of Hg_2Cl_2 and $(CN)_2$. Although the thermal decompositions of $KHg(CN)_2Br$ and $KHg(CN)_2I$ also occur partially according to the firs ttype, the main bulk of the material decomposes by the second route. Peaks corresponding to the decomposition products of both reaction types can be identified on the DTA curves, and in addition the presence of small amounts of $(CN)_2$ and Hg_2Br_2 or Hg_2I_2 could be detected. However, the weight loss derived from the TG curves corresponded predominantly to the thermal decomposition leading to $Hg(CN)_2$ + KX.

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RÉSUMÉ — On a étudié la décomposition thermique de $Hg(CN)_2$, $K_2Hg(CN)_4$, $KHg(CN)_2Cl \cdot H_2O$, $KHg(CN)_2Br$ et $KHg(CN)_2I$. Les résultats ont montré que chacun des complexes étudiés se décompose à une température inférieure à celle de $Hg(CN)_2$ lui-même. Les complexes contenant des halogènes se décomposent suivant deux voies. Avec $KHg(CN)_2Cl \cdot H_2O$ c'est la liaison Hg—CN qui est rompue la première et il se forme $Hg_2Cl_2(CN)_2$ et KCN. Avec $KHg(CN)_2Br$ et $KHg(CN)_2I$, la première étape de la décomposition est celle de $Hg(CN)_2$ et de KBr ou KI.

ZUSAMMENFASSUNG — Die thermische Zersetzung von $Hg(CN)_2$, $K_2Hg(CN)_4$, $KHg(CN)_2Cl \cdot H_2O$, $KHg(CN)_2Br$ und $KHg(CN)_2I$ wurde studiert. Die Ergebnisse zeigten, daß jede der untersuchten Komplexverbindungen bei niedrigeren Temperaturen zersetzt wird, als $Hg(CN)_2$ selbst. Die halogenhaltigen Komplexe werden auf zweierlei Arten zersetzt. Im $KHg(CN)_2Cl \cdot H_2O$ wird zuerst die Bindung Hg—CN gespalten, wobei Hg_2Cl_2, $(CN)_2$ und KCN entstehen. Andererseits ist die erste Zersetzungsstufe bei $KHg(CN)_2Br$ und $KHg(CN)_2I$ die Zersetzung zu $Hg(CN)_2$ und KBr bzw. KI.

Резюме — Изучен терморaспад $Hg(CN)_2$, $K_2Hg(CN)_4$, $KHg(CN)_2Cl \cdot H_2O$, $KHg(CN)_2Br$ и $KHg(CN)_2I$. Установлено, что каждый из изученных комплексов распадается при более низкой температуре, чем сам $Hg(CN)_2$. Галоген-содержащие комплексы распадаются но двум путям. В $KHg(CN)_2Cl \cdot H_2O$ первой рвется связь Hg—CN и образуются Hg_2Cl_2, $(CN)_2$ и KCN. При распаде же $KHg(CN)_2Br$ и $KHg(CN)_2I$ первой ступенью является образование $Hg(CN)_2$ и KBr или KI.