Thermochimica Acta, 110 (1987) 373–381
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

DECOMPOSITION OF INORGANIC COMPOUNDS

NARENDER KUMAR KAUSHIK

Department of Chemistry, University of Delhi, Delhi 110 007 (India)

ABSTRACT

Selected papers from the session on decomposition of inorganic compounds are reviewed and discussed.

A thermoanalytical study of $(NH_4)_2Cd_2(SO_4)_3$, an intermediate compound in the heating of the mixture $(NH_4)_2SO_4$–$CdCO_3$ (1 : 1, w/w) was discussed by Garcia-Clavel and Servert-Buxados [1]. As the isolation of $(NH_4)_2Cd_2(SO_4)_3$ is not possible during the course of this decomposition reaction, the authors synthesized it in the laboratory. The thermogram of $(NH_4)_2Cd_2(SO_4)_3$ does not show any sudden change (Fig. 1). The decomposition range is 220–440 or 175–430°C at heating rates of 300 or 150°C

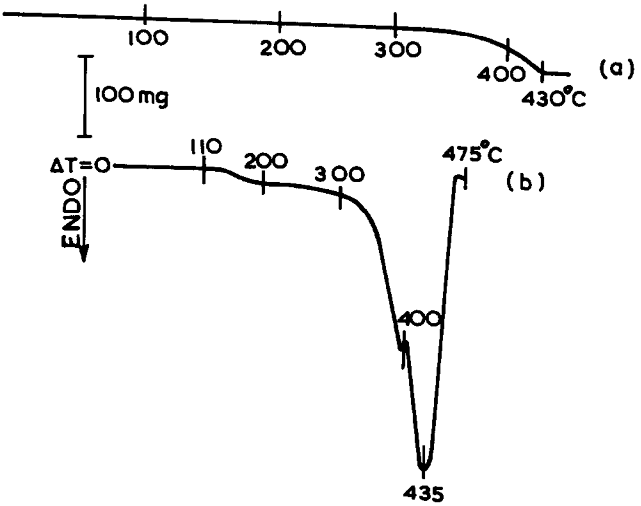

Fig. 1. (a) TG and (b) DTA curves at 150°C h^{-1}.

Thermal Analysis Highlights, 8th ICTA, Bratislava, Czechoslovakia.

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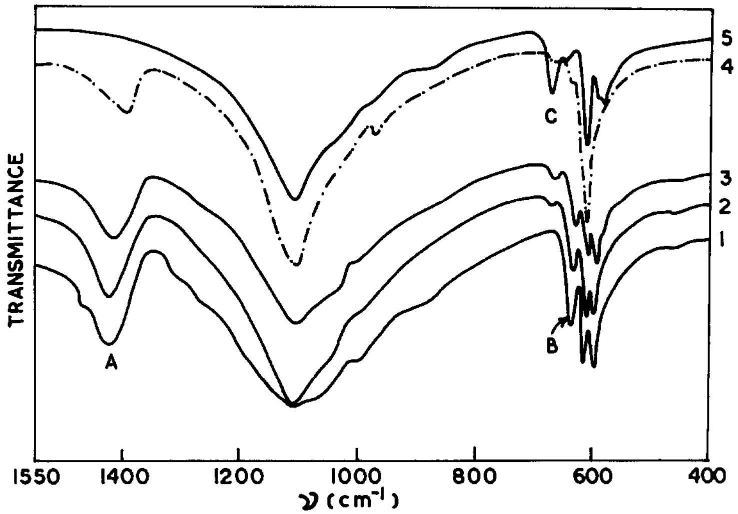


Fig. 2. IR spectra of samples taken at (1) 175, (2) 350, (3) 375, (4) 400 and (5) 500 °C in the TG curve at 150 °C h^{-1}.

h^{-1}, respectively. The infrared spectra taken at different temperatures in these ranges show progressive decreases in the first band of NH_4^+ and a second band of $(NH_4)_2Cd_2(SO_4)_3$ and the appearance of a third band belonging to $CdSO_4$ (Fig. 2). In the X-ray diffractogram of the sample at 350, 375 and 400 °C the authors identified the double sulphate, $CdSO_4 \cdot (NH_4)_2SO_4$, whereas the X-ray diffractogram of the residue at 500 °C corresponds to anhydrous $CdSO_4$. The DTA of the compound was recorded at a lower heating rate in order to separate all the possible consecutive steps. There is a small peak at 400 °C that cannot be separated from the large decomposition peak even using slower heating rates.

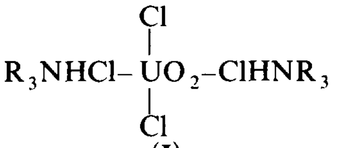
Sato and Takahashi [2] described the thermal decomposition of solvent-extracted chloro complexes of uranium(VI) with trioctylamine and trioctylmethylammonium chloride. The complexes $(R_3NH)_2UO_2Cl_4$ and $(R_3R'N)_2UO_2Cl_4$, prepared by drying in vacuo the organic solution from the extraction of aqueous UO_2Cl_2 solution with trioctylamine (TOA, R_3N) and trioctylmethylammonium chloride (TOMAC, $R_3R'NCl$) in benzene, were examined by thermogravimetry and differential thermal analysis under an atmosphere of N_2 and their thermal decomposition products, such as volatile matter and residues, by gas chromatography, X-ray diffraction and infrared spectroscopy. It was found that the complexes with TOA and TOMAC are thermally decomposed to UO_2 at 320–360 and 280–325 °C via UO_2Cl_2 formed by cracking of the complexes at 205–320 and 200–280 °C, respectively. The following decomposition mechanisms were proposed:

$$(R_3NH)_2UO_2Cl_4 \xrightarrow[-\text{HCl, cracking}]{250\text{–}320\,°\text{C}} UO_2Cl_2 \xrightarrow[\text{dechlorination}]{320\text{–}360\,°\text{C}} UO_2$$

and

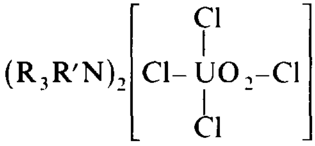
$$(R_3R'N)_2UO_2Cl_4 \xrightarrow[-CH_3Cl,\ \text{cracking}]{200-280\,^\circ C} UO_2Cl_2 \xrightarrow[\text{dechlorination}]{280-325\,^\circ C} UO_2$$

supporting the structures **I** and **II** for uranyl complexes with TOA and TOMAC, respectively.



$$R_3NHCl-\underset{Cl}{\overset{Cl}{UO_2}}-ClHNR_3$$

(**I**)



$$(R_3R'N)_2\left[Cl-\underset{Cl}{\overset{Cl}{UO_2}}-Cl\right]$$

(**II**)

The thermal decomposition of some substituted cadmium(II) salicylato complexes was reported by Kokkonen et al. [3]. The authors prepared hydrous cadmium(II) salicylate and also 5-chloro, 5-bromo, 5-iodo and 5-nitrosalicylato complexes and characterized them on the basis of elemental analysis and IR studies. The thermal behaviour of these complexes was studied by TG and DTG techniques. The results of thermal analysis, mass spectrometry and scanning electron microscopy revealed that the decomposition of these complexes involves three or four stages, depending on the complexes. The first decomposition stage takes place at 323–418 K and corresponds to the dehydration of two water molecules (Fig. 3). The second step, at 418–598 K, corresponds to the loss of ligand acid, while in the third step the loss of one ligand acid molecule takes place in the case of the cadmium salicylato complex. For the 5-substituted cadmium salicylato complexes the third and fourth stages partly overlap. Mass spectrometric and scanning electron microscopic results showed that during these stages the decomposition products contain partly ligand acid but cadmium halides ($CdCl_2$, $CdBr_2$ and CdI_2) are also present. With the 5-iodosalicylato complex the third and fourth stages overlap completely, whereas for the 5-chloro- and 5-bromosalicylato complexes loss of $CdBr_2$ or $CdCl_2$, respectively, begins slightly later. Scanning electron microscopy of the solid decomposition residue of 5-bromosalicylato complexes at 723 K showed the presence of crystals of $CdBr_2$ and amorphous CdO.

The final decomposition product of these complexes is CdO, excluding the 5-iodosalicylato complex, where all the cadmium disappears as CdI_2.

The following decomposition scheme for the 5-bromosalicylato complex was proposed:

$$Cd(5\text{-}Br\text{-}Sal)_2\cdot 2H_2O \xrightarrow[-H_2O]{\text{Step I}} Cd(5\text{-}Br\text{-}Sal)_2 \xrightarrow[\text{5-Br-Sal}]{\text{Step II}} Cd(5\text{-}Br\text{-}Sal)^+$$
$$\xrightarrow[\text{5-Br-Sal}+CdBr_2]{\text{Step III-IV}/O_2\ (\text{air})} CdO$$

For the 5-nitro complex, which was found to decompose explosively, only the loss of water molecules, having a maximum at 355 K, was determined.

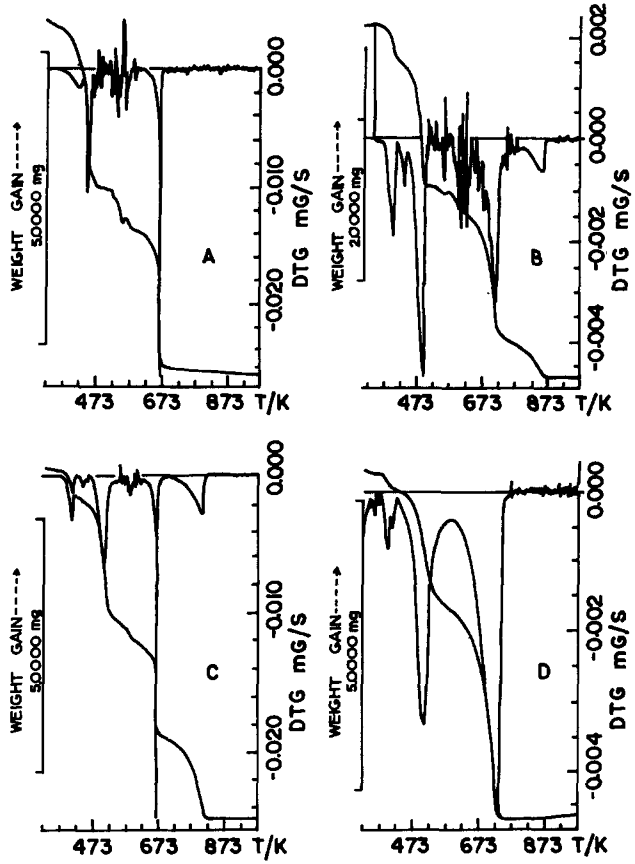


Fig. 3. TG and DTG plots of (A) bis(2-hydroxybenzoato)cadmium(II) dihydrate, (B) bis(2-hydroxy-5-chlorobenzoato)cadmium(II) dihydrate, (C) bis(2-hydroxy-5-bromobenzoato)cadmium(II) dihydrate, and (D) bis(2-hydroxy-5-iodobenzoato)cadmium(II) dihydrate.

The thermal behaviour of tris-*N*-(*o*-, *m*- and *p*-chlorophenyl)dithiocarbamato complexes was investigated by Kaushik et al. [4] using TG and DTA techniques in a static air atmosphere.

The TG curves of Au(III) complexes show a two-step decomposition (Fig. 4). The first decomposition step corresponds to the formation of gold sulphide while the second step results in the formation of metallic gold. The DTA curves (Fig. 5) of the complexes show one endotherm and two exotherms. The first endotherm corresponds to the fusion of the complex and the two exotherms are due to the decomposition of dithiocarbamate to sulphide and conversion of sulphide to metallic gold:

$$\mathrm{Au[S_2CNH(ClC_6H_4)]_3} \xrightarrow{\text{Step I}} \mathrm{Au_2S_3} \xrightarrow{\text{Step II}} \mathrm{Au}$$

The thermogram of As(III) complexes shows two major thermal changes,

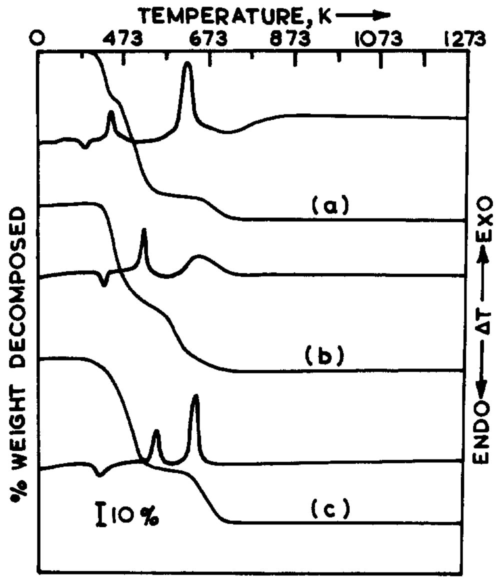


Fig. 4. TG and DTA curves of (a) $Au(OCD)_3$, (b) $Au(MCD)_3$ and (c) $Au(PCD)_3$.

viz., decomposition of dithiocarbamate to sulphide and volatilization of sulphide. The crucible was empty at 883 K. The DTA profiles of the complexes show two endotherms and two exotherms. The first endotherm

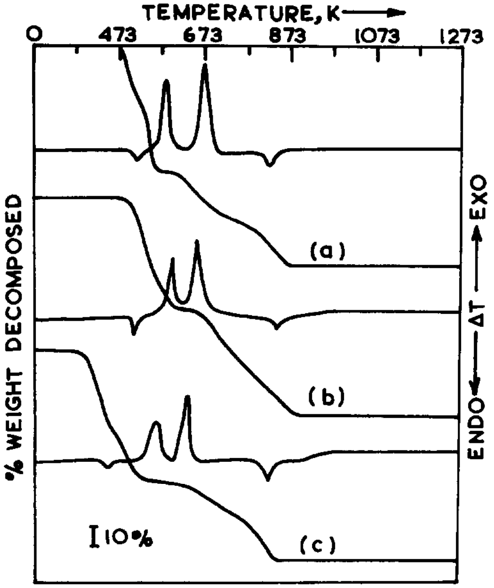


Fig. 5. TG and DTA curves of (a) $As(OCD)_3$, (b) $As(MCD)_3$ and (c) $As(PCD)_3$.

might be due to the fusion of the complexes. The two exotherms could be due to the decomposition of the complexes to the sulphides, which probably takes place in two consecutive steps that are not resolved in the TG curves. The last endothermic band might represent the sublimation of the sulphide formed after first weight loss step.

$$As[S_2CNH(ClC_6H_4)]_3 \xrightarrow{\text{Step I}} As_2S_3 \xrightarrow{\text{Step II}} \text{volatilization}$$

The thermal behaviour of a number of titanyl and zirconyl oxalates has been discussed and all this work was summarized in the form of a review by Sharma and Kaushik [5].

Kaushik et al. [6] discussed the thermal decomposition of pyridinium, zirconyl and hafnyl oxalates. The decomposition proceeds through three steps, viz., dehydration, decomposition of anhydrous oxalate to an intermediate, $ZrO_2/HfO_2 \cdot X(C_5H_5N)$, and finally decomposition of this intermediate to oxide (Figs. 6 and 7).

$$(C_5H_5NH)_2MO(C_2O_4)_2 \cdot 2H_2O \rightarrow (C_5H_5NH)_2MO(C_2O_4)_2 + 2H_2O \qquad \text{(I)}$$

$$(C_5H_5NH)_2MO(C_2O_4)_2 \rightarrow MO_2 \cdot X(C_5H_5N) + H_2O + (2-x)C_5H_5N + 2CO_2 + 2CO \qquad \text{(II)}$$

$$2CO + O_2 \rightarrow 2CO_2$$

$$MO_2 \cdot XC_5H_5N \rightarrow MO_2 + C + \text{decomp. product of pyridine} \qquad \text{(III)}$$

$$C + O_2 \rightarrow CO_2$$

($x = 1.29$ when M = Zr, $x = 1.24$ when M = Hf).

Both of the hydrated oxalates were dehydrated in a single-step process.

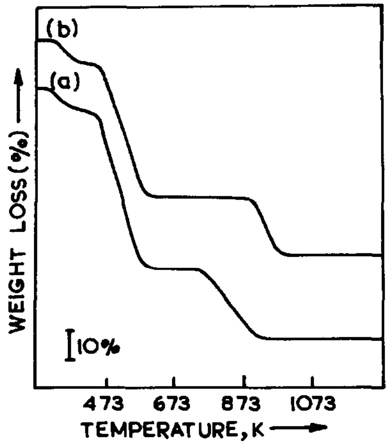


Fig. 6. TG curves of (a) $(C_5H_5NH)_2ZrO(C_2O_4)_2 \cdot 2H_2O$ and (b) $(C_5H_5NH)_2HfO(C_2O_4) \cdot 2H_2O$.

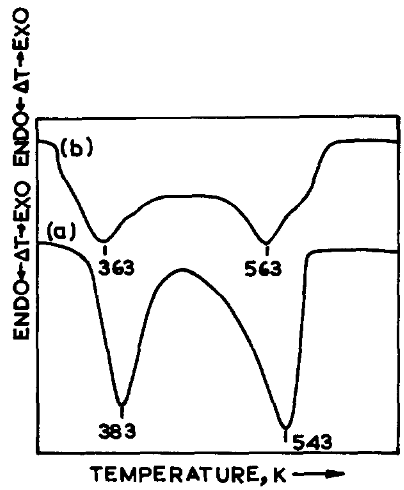


Fig. 7. DTA curves of (a) $(C_5H_5NH)_2ZrO(C_2O_4)_2 \cdot 2H_2O$ and (b) $(C_5H_5NH)_2HfO(C_2O_4) \cdot 2H_2O$.

The expected endothermic behaviour associated with the dehydration process was observed from DTA curves in almost the same temperature ranges.

Anhydrous oxalate decomposition is a complicated endothermic process. Infrared spectra of this decomposition step show that the oxalate peaks disappears slowly while the peaks for free pyridine become observable. This means that part of the liberated pyridine stays strongly adsorbed by ZrO_2/HfO_2. No formation of carbonate could be detected.

The decomposition of the intermediate pyridine adduct to oxide is also a single-step process in both complexes. No DTA curve corresponding to this decomposition was obtained owing to the limited range available with the instrument employed.

Dollimore et al. [7] reported the preparation of single crystals of $SrC_2O_4 \cdot 2H_2O$ and $SrC_2O_4 \cdot H_2O$, and thermal decomposition of these compounds was studied using TG in both the isothermal and rising temperature modes, DTA, infrared spectroscopy and evolved gas pressure measurements. Anhydrous SrC_2O_4 in a polycrystalline form decomposes into strontium carbonate and CO:

$$SrC_2O_4 \rightarrow SrCO_3 + CO$$

which was demonstrated by TG, DTA and infrared spectroscopy.

There is a gaseous secondary reaction:

$$2CO \rightleftarrows C + CO_2$$

but in an oxidizing atmosphere the CO and C can be oxidized to CO_2. These side reactions are exothermic and could alter the kinetics of the main reaction, causing temperature gradients inside the sample. This is supported by a comparison of DTA and TG curves in air and an inert atmosphere. The DTA and TG data in both air and N_2 showed that the decomposition of the SrC_2O_4 derived from the dehydration of $SrC_2O_4 \cdot H_2O$ takes place at higher temperatures than those for SrC_2O_4 derived from the polyhydrate salt. This was due to the different dehydration processes arising from the individual crystalline structures and the water content of the starting hydrated oxalates.

The thermal properties of $NH_4HV_6O_{16} \cdot 3H_2O$ and $KHV_6O_{16} \cdot 3H_2O$ were investigated by Ulická and Zurkova [8]. $NH_4HV_6O_{16} \cdot 3H_2O$ loses three molecules of water and probably part of the ammonium content also within the temperature range 40–270 °C. It follows from the IR spectra and X-ray powder patterns that the original structure of the substance is preserved up to 270 °C. The complicated exothermic process between 270 and 380 °C is connected with a loss of ammonium and constitutional water and with the formation of V_2O_5.

With $KHV_6O_{16} \cdot 3H_2O$, continuous dehydration takes place with the temperature range 20–330 °C. It was found that this compound decomposes primarily to KVO_3 and V_2O_5, which react together to form bronzes [9] of various composition. The factors that influence the composition of the product of the thermal decomposition are so far unknown.

Garcia-Clavel et al. [10] studied the preparation and thermal decomposition of lead trioxynitrate. This compound was prepared by precipitation at 0 °C from a 0.75 M solution of lead nitrate with concentrated ammonia solution. In the TG curve, the first release corresponds to the dehydration of lead trioxynitrate. The second release, between 250 and 550 °C, corresponds to the decomposition of anhydrous trioxynitrate to PbO, which occurs in two steps with the intermediate formation of lead pentoxynitrate, as the X-ray diffraction confirms.

$$Pb(NO_3)_2 \cdot 3Pb(OH)_2 \rightarrow Pb(NO_3)_2 \cdot 3PbO \rightarrow Pb(NO_3)_2 \cdot 5PbO \rightarrow PbO$$

The thermal decomposition of the complexes of general formula $Co(NH_3)_6MF_6$ was investigated by simultaneous TG and DTA by Demšar and Bukovec [11]. X-ray powder measurements and IR spectroscopy were employed to characterize the intermediate and final products. The thermal decomposition of the compounds with M = Sc and Mn takes place in one step to give finally $CoF_2 + ScF_3$ and $CoF_2 + MnF_2$, respectively. The number of DTA effects can be correlated with the reduction of Co(III) in the Sc compound and to the reduction of Co(III) and Mn(III) in the Mn complex. The compounds with M = Al, Ga, V, Cr and Fe all decompose in two steps. In the first stage the reduction of Co(III) to Co(II) takes place to yield the intermediate composition NH_4CoMF_6 with cubic unit cells.

$$6Co(NH_3)_6MF_6 \rightarrow 6NH_4CoMF_6 + N_2 + 28NH_3$$

Further decomposition proceeds by giving off NH_4F and leaving a mixture of $CoF_2 + MF_3$ or $CoF_2 + MF_2$.

The thermal decomposition of copper(I) sulphate, which was studied by Debinski [12], is a three-stage endothermic process, Cu and $CuSO_4$ being the main decomposition products in the first stage (above 420 K). The second stage is associated with the formation of Cu_2O in the range 575–646 K. In the third stage of decomposition, taking place above 726 K, unreacted Cu and Cu_2SO_4 react completely to form Cu_2O.

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