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THERMAL DECOMPOSITION OF COPPER(II) BENZENETRICARBOXYLATES IN AIR ATMOSPHERE

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The conditions of thermal decomposition of copper(II) benzenetricarboxylates in air atmosphere at heating rates of 10 and 5 deg·min^{-1} were studied. At 10 deg·min^{-1}, the hemimellitate and trimesinate of copper(II) lose crystallization water and then decompose directly to CuO, whereas at 5 deg·min^{-1} they decompose to CuO through Cu_2O. The trimellitate of copper(II) heated at various rates decomposes in the same way: it loses 1 water molecule and then decomposes directly to CuO.

Metal complexes of benzenetricarboxylic acids are little known. Graabe and Leonhard [1] obtained hemimellitates of K, Ag and Ba as 3-substitution salts sparingly soluble in water. Yasuda [2] studied the stability constants of Cu(II) and Ni(II) complexes of hemimellitic acid. Barth and Schreder [3] prepared trimellitates of Ag(I) and Ba. Trimesinic acid complexes of Na, K, Cu(II), Ag(I), Ba, Zn and Pb(II) are known. Trimesinates of Cu(II), Ag(I), Ba, Zn and Pb(II) have been prepared as 3-substitution salts. As a continuation of our work on the thermal decomposition of transition and inner-transition element carboxylates, we now report the thermal decomposition of copper(II) benzenetricarboxylates in air atmosphere.

Experimental

Complexes of copper(II) with hemimellitic, trimesinic and trimellitic acids were prepared by adding an equivalent amount of a 0.1 *M* solution of $Cu(NO_3)_2$ to a hot solution of ammonium benzenetricarboxylate (pH 5–5.7). The precipitate formed was heated in the mother liquor for 0.5 h, then filtered off, washed with distilled water to remove NH_4^+ ions and dried at 303 K to constant weight. The prepared complexes of copper(II) are blue crystalline solids sparingly soluble in water.

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The contents of carbon and hydrogen in the prepared complexes were determined by elemental analysis. The copper content was determined by polarography, ignition to CuO and via the TG curve (Table 1). The hemimellitate, trimesinate and trimellitate of copper(II) were prepared as hydrates with a metal to ligand ratio of 3 : 2.

Table 1 Analytical data

Complexes of Cu(II)		Cu, %		C, %		H, %	
Name	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found
Hemimellitate 1, 2, 3	$Cu_3(C_9H_3O_6)_2 \cdot 2H_2O$	29.75	30.2	33.70	32.9	1.56	1.9
Trimesinate 1, 3, 5	$Cu_3(C_9H_3O_6)_2 \cdot 3H_2O$	28.94	28.9	32.79	31.8	1.82	2.0
Trimellitate 1, 2, 4	$Cu_3(C_9H_3O_6)_2 \cdot 5H_2O$	27.09	27.1	31.1	32.0	2.30	2.4

The IR spectra of the studied complexes were recorded in the range 4000–400 cm^{-1}. Analysis of the IR spectra confirmed the compositions of the complexes.

The thermal stabilities of the complexes were studied; the TG, DTG and DTA curves were recorded. The measurements were made on an OD–102 derivatograph at heating rates of 10 and 5 deg·min^{-1}. The samples were heated in air, at sensitivity results.

The results are given in Tables 2 and 3 and Figs 1–3. The decomposition products were calculated from the weight losses in the TG curves and during isothermal decomposition, and were confirmed by recording the IR spectra. When heated at various rates, benzenetricarboxylates of copper(II) decompose in various ways. The thermal decompositions of these complexes when heated at a rate of 10 deg·min^{-1} are illustrated in Table 2. Copper(II) benzenetricarboxylates decompose in two stages. Dihydrated hemimellitate first loses its crystallization water, to the accompaniment of an endothermic effect, and next the anhydrous complex is transformed into CuO. Copper(II) trimesinate and trimellitate lose one water molecule and then decompose to CuO.

The thermal decompositions of the complexes at a heating rate of 5 deg·min^{-1} are illustrated in Table 3. Copper(II) hemimellitate and trimesinate decompose in three steps. They lose crystallization water at 313–493 K, and then decompose to CuO with the intermediate formation of Cu_2O. Copper(II) trimellitate decomposes in two steps in the same way as at 10 deg·min^{-1}. The final product of all benzenetricarboxylate decompositions is CuO, which forms at 673–853 K at 5 deg·min^{-1} and at 853–943 K at 10 deg·min^{-1}.

Table 2 Data of thermal decomposition of copper(II) benzenetricarboxylates at heating rate 10 deg·min^{-1}

Complexes of Cu(II)		Temperature range of dehydration, K	Loss of H_2O mole	Loss of weight, %		Temperature range of decomposition K	Loss of weight, %		Temperature of CuO formation, K
Name	Formula			Calcd.	Found		Calcd.	Found	
Hemimellitate	$Cu_2L_2 \cdot 2H_2O$	333–573	2	5.6	5.5	573–853	62.7	63.0	853
Trimesinate	$Cu_3L_2 \cdot 3H_2O$	333–393	1	2.7	3.0	553–913	63.7	62.5	913
Trimellitate	$Cu_3L_2 \cdot 5H_2O$	353–433	1	2.5	2.5	473–943	66.0	66.1	943

Table 3 Data of thermal decomposition of copper(II) benzenetricarboxylates at heating rate 5 deg·min^{-1}

Complexes of Cu(II)		ΔT_1, K	Loss of weight, %		Loss of H_2O mole	ΔT_2, K	Loss of weight, %		ΔT_3, K	Loss of weight, %		T_k
Name	Formula		Calcd.	Found			Calcd.	Found		Calcd.	Found	
Hemimellitate	$Cu_3L_2^x \cdot 2H_2O$	323–453	5.6	6.0	2	513–673	65.8	64.5	673–853	62.8	63.0	853
Trimesinate	$Cu_3L_2 \cdot 3H_2O$	313–493	5.5	5.0	2	513–668	67.4	65.0	668–743	63.7	63.5	743
Trimellitate	$Cu_3L_2 \cdot 5H_2O$	353–433	2.56	2.5	1	—	—	—	473–943	66.0	66.1	943

L^x – $C_9H_3O_6^{3-}$

ΔT_1 – Temperature range of dehydration

ΔT_2 – Temperature range of decomposition to Cu_2O

ΔT_3 – Temperature range of oxidation of Cu_2O to CuO

T_k – Temperature of CuO formation

References

1 P. Graabe and S. Leonhardt, Ann., 290 (1889) 218.
2 M. Yasuda, Z. Phys. Chem., 27 (1961) 333.
3 L. Barth and J. Schreder, Ber., 12 (1879) 1252.
4 Beilsteins Handbuch der organischen Chemie, Verlag I. Springer, Berlin 1933.
5 W. Brzyska and A. Kula, J. Thermal Anal., 25 (1983) 531.
6 W. Brzyska, R. Kurpiel-Gorgol and M. Dabkowska, J. Thermal Anal., 28 (1983) 333.
7 W. Brzyska and W. Ożga, J. Thermal Anal., 23 (1982) 231.