

Short Communications

THERMAL DECOMPOSITION OF HYDRATED IRON(II) OXALATE AND MANGANESE(II) OXALATE IN VACUUM

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The thermal decomposition of hydrated iron(II) oxalate and manganese(II) oxalate under high vacuum conditions ($\sim 10^{-5}$ mm Hg) has been studied by differential thermal analysis. The decomposition in vacuum of iron(II) oxalate is exothermic, while that of manganese(II) oxalate is endothermic. An explanation is offered for this behaviour.

The thermal decomposition of transition metal oxalates in air and in inert atmospheres has been studied by many workers [1-4]. The results reported in the literature on the decomposition of iron(II) oxalate are conflicting. Macklen [2] has reported the decomposition in an atmosphere of nitrogen to be endothermic occurring around 320° , while Brown and Bevan [1] have observed an exothermic decomposition at 220° under similar conditions. Although the decomposition of transition metal oxalates has been studied in air and in different gaseous atmospheres, the decomposition under high vacuum conditions of these compounds does not seem to have been investigated. It is expected that such a study will clarify the controversy regarding the iron(II) oxalate decomposition and throw more light on oxalate decomposition in general. With this end in view, the thermal decomposition of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ has been studied under vacuum (both dynamic and static) by the differential thermal analysis (DTA). The results are presented in this paper.

Experimental

$\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ were prepared by the standard method [3] and the composition ascertained by chemical analysis of metal and oxalate. The DTA study of the compound (~ 100 mg) was carried out in both dynamic and static vacuum conditions ($\sim 10^{-5}$ mm Hg) in a manual DTA apparatus employing chromel-alumel thermocouples. In the dynamic vacuum studies the DTA was carried out when the system was being continuously evacuated, while under static conditions the system was first evacuated to the desired vacuum, then isolated, and the DTA carried out. The vacuum was obtained by using a mercury diffusion pump backed with a rotary pump. Ignited alumina was used as the ref-

erence material. The heating rate was $8 \pm 1^\circ$ per minute. The emf's corresponding to the sample temperature and the differential temperature were measured with a sensitive DC microvoltmeter. It was found that there was no significant difference between the results obtained under dynamic and static vacuum conditions for both compounds. This is not surprising in view of the fact that the total volume of the DTA unit was fairly high such that the gases evolved during decomposition

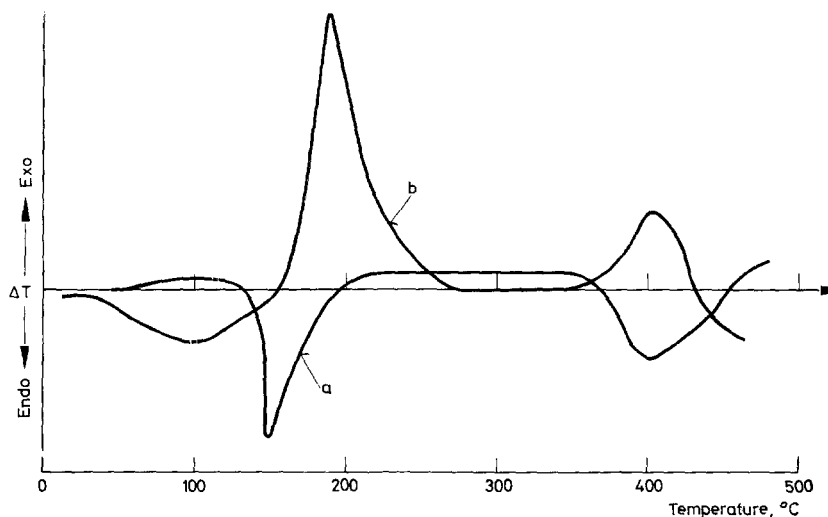


Fig. 1. DTA curves of a) $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; b) $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in vacuum ($\sim 10^{-5}$ mm Hg)

would be expected to exert negligible pressure. Typical DTA curves obtained under dynamic conditions are given in Fig. 1. The X-ray powder pattern of the decomposition product of iron(II) oxalate was obtained using Fe K_α radiation.

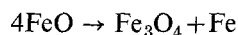
Results and discussion

The DTA curve of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ obtained under vacuum conditions is similar to that obtained in nitrogen atmosphere by Brown and Bevan [1], showing endothermic dehydration in the temperature range $60 - 140^\circ$ followed by the exothermic decomposition of the anhydrous oxalate around 200° . There is another exotherm around 380° . However, as seen in Fig. 1, the decomposition of MnC_2O_4 under similar conditions occurs endothermally around 380° . Our studies on other divalent transition metal oxalates [except Cu(II)] reveal that the decomposition process in vacuum and in inert atmospheres is usually endothermic, iron(II) oxalate being the exception [6].

The decomposition of a divalent transition metal oxalate may follow either of the two routes [4, 7]



The process (1) gives rise to an endothermic effect in the absence of any other complicating side reactions. The observation of an exotherm for the decomposition of ferrous oxalate can only be associated with a highly exothermic secondary reaction, which masks the usual endothermic effect of the decomposition. The primary decomposition product FeO is thermodynamically unstable below 573° and disproportionates as follows:



The ΔH of this reaction is around -70 Kcal mole⁻¹ as calculated from the values of standard heats of formation [8]. It is possible that the exothermicity of this reaction masks the endothermic decomposition giving rise to an overall exotherm in the DTA. The second exothermic effect may be attributed to the crystallisation and phase transformation of amorphous Fe₃O₄ [4]. The X-ray diffraction pattern of the final product obtained in vacuum reveals the presence of Fe₃O₄ and α -Fe. This is in accord with the proposed mechanism of decomposition. The final product of decomposition, in vacuum, of manganese(II) oxalate was found to be MnO as evidenced by its greenish colour and also identified by chemical analysis. The chemical analysis indicated the absence of any other higher oxidation states of manganese.

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