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Note

Gas chromatographic study of the thermal decomposition of oxalates

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Although the decomposition of solid oxalates is usually studied by thermogravimetric analysis (TGA)¹⁻⁴, GC analysis of the gaseous products offers advantages, particularly for transition metal oxalates. The various steps in their decomposition often overlap and a mixture of gases is evolved, the composition of the mixture and of the residual product depending upon temperature. In TGA, these aspects are often not revealed and consequently the complexity of the decomposition is overlooked. The present work illustrates the applicability of GC in elucidating the mechanism of the decomposition of a few typical transition metal oxalates, namely those of Mn, Pb, Zn, Co, Ni, Cu and Fe.

EXPERIMENTAL AND RESULTS

The various oxalates are prepared by precipitation from solutions of salts of the metals by potassium oxalate. The precipitates are filtered off and washed with distilled water and then ethanol. They are dried at 100° and kept in a vacuum desiccator over phosphorus pentoxide for several days. Their purity is checked by dissolving weighed amounts in hot dilute sulphuric acid and titrating the solutions against standardised potassium permanganate. The purity is in the range of 99.5-99.8%.

The decomposition is carried out in an oven represented in Fig. 1. A brass tube B, of 30 cm length and 2.5 cm-diameter, is enclosed in a glass tube G, which is electrically heated by a Nichrome wire N which is wound over it. By passing a controlled current through the heater wire, the oven can be maintained at any desired temperature as measured by a thermometer T. The sample to be studied is spread uniformly on a 20 × 2 cm aluminium strip A, and placed at the centre of the oven. A stream of nitrogen can be passed through the oven by inlet and outlet tubes in stoppers fitted at the two ends:

In each experiment, the oven is maintained at the desired temperature for half an hour and 2.5 g of the oxalate sample is mixed with 15 g of dry, powdered sand and introduced into the oven. A slow stream of nitrogen is passed and the gaseous decomposition products are swept out and dried over anhydrous calcium chloride in D and led into the gas sampling valve of a Beckman GC-2 gas chromatograph. The gases enclosed in the sampling valve are led into the column and peaks for the various components are recorded. Nitrogen is used as the carrier gas at an inlet pressure of

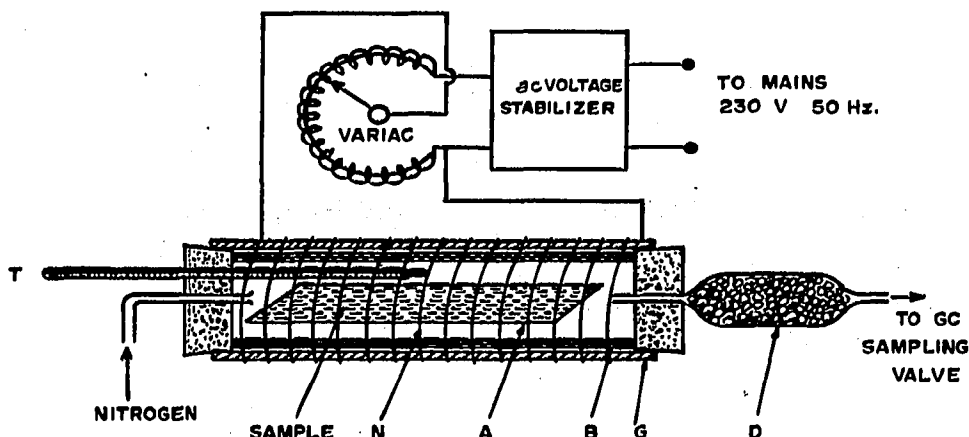


Fig. 1. Oven for thermal decomposition of oxalates.

1.75 kg/cm² and a flow-rate of 52 ml/min. The column is a 2 m × 6 mm I.D. copper tube packed with Chromosorb 102 (60–80 mesh) and maintained at 40°. The detector is a thermal conductivity cell with a filament current of 150 mA. The signals are recorded on a Bristol Dynamaster recorder with a sensitivity of 1 mV for full-scale deflection.

The gaseous products from the decomposition of these oxalates are carbon monoxide and carbon dioxide; any trace of moisture evolved is retained by the anhydrous calcium chloride. The detector responses for the two gases are compared by leading the pure gases separately through the gas sampling valve and noting the individual peaks. From the ratio of these peaks (0.26) and from the ratio of the peaks for the two gases in the decomposition product, the ratio of their partial pressures,

TABLE I

THERMAL DECOMPOSITION OF OXALATES

Variation of partial pressure ratio, P_{CO}/P_{CO_2} , with temperature. Ratio of the detector response for CO and CO₂ = 0.26.

Oxalate	Temperature (°C)	Ratio of the peak heights, CO/CO ₂	Partial pressure ratio, P_{CO}/P_{CO_2}
MnC ₂ O ₄	300	3.1 ± 0.1	11.9
	306	3.7	14.2
	315	4.6	17.7
	320	5.3	20.4
PbC ₂ O ₄	328	0.82 ± 0.02	3.2
	333	0.89	3.4
	340	1.00	3.9
	346	1.30	4.8
ZnC ₂ O ₄	310	3.9 ± 0.1	15.0
	320	4.0	15.4
	328	4.2	16.1
	335	4.3	16.5
CoC ₂ O ₄	323	0.12 ± 0.02	0.46

P_{CO}/P_{CO_2} , is obtained by dividing the latter ratio by the former. This ratio is confirmed by repeating the analysis several times.

The experiment is repeated at different temperatures and each time the ratio P_{CO}/P_{CO_2} is determined. Similar studies are carried out with all the other oxalates. The results are presented in Tables I and II.

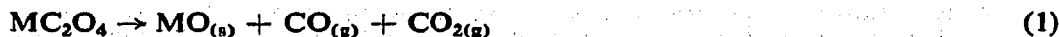
TABLE II

THERMAL DECOMPOSITION OF OXALATES IN NITROGEN
Gaseous products analysed by GC.

Oxalate	Decomposition range ($^{\circ}C$)	Gaseous products
MnC_2O_4	300–320	CO, CO ₂
PbC_2O_4	328–346	CO, CO ₂
ZnC_2O_4	310–335	CO, CO ₂
CoC_2O_4	310–330	CO, CO ₂
NiC_2O_4	300–320	CO ₂
CuC_2O_4	250–265	CO ₂
FeC_2O_4	220–245	CO ₂

DISCUSSION

The experiments showed that the oxalates under study can be classified into two groups, one yielding carbon monoxide and carbon dioxide simultaneously (oxalates of Mn, Zn, Pb and Co), while the other yields only carbon dioxide. In the decomposition of manganese oxalate, which is typical of the first group, the ratio P_{CO}/P_{CO_2} is 11.9 at 300° over a considerable range of the decomposition. From the TGA of this and a few other oxalates (denoted as MC_2O_4), Dollimore *et al.*² suggested that the mechanism of decomposition is



This reaction would imply an equimolar proportion of CO and CO₂, which is, in fact, not observed in the GC analysis of the gaseous products. Another plausible mechanism is



followed by



The observed overwhelming proportion of CO would imply that reaction 2 occurs predominantly over reaction 3, but this would then lead to an accumulation of MCO₃, which, by reaction 3, should increase the yield of CO₂, so that the P_{CO}/P_{CO_2} ratio should decrease continuously during the decomposition. The ratio is observed to be constant, however, and in view of this it appears that reactions 1 and 2 occur simultaneously but independently, the latter occurring predominantly over

reaction 1 while reaction 3 occurs only to a negligible extent. This scheme can account for the overwhelming proportion of CO and also for the constancy of the $P_{\text{CO}}/P_{\text{CO}_2}$ ratio.

The $P_{\text{CO}}/P_{\text{CO}_2}$ ratio in fact increases with temperature, so that at higher temperatures reaction 2 occurs even more readily than reaction 1. At such temperatures, owing to the greater overwhelming proportion of CO, there is a greater accumulation of MCO_3 , yet the constancy of the $P_{\text{CO}}/P_{\text{CO}_2}$ ratio suggests that reaction 3 occurs to a negligible extent.

From the TGA of lead and cobalt oxalates², it is reported that the end products are the respective metals and the decompositions occur by the reaction



The GC analysis of the gaseous products clearly shows the presence of CO and therefore there is evidently some formation of oxide. The $P_{\text{CO}}/P_{\text{CO}_2}$ ratio for lead oxalate at 328° is 3.2 and therefore reaction 4 is indeed less predominant than reaction 2. On the other hand, for cobalt oxalate at 323°, the ratio is 0.46, which suggests that reaction 4 is important.

The second group includes oxalates of Fe, Ni and Cu, which yield only CO_2 as the gaseous product. The reaction can therefore be represented by reaction 4, in agreement with the TGA results².

In conclusion, it should be emphasized that were it not for the GC analysis of the gaseous products in the decomposition of oxalates, the complexity of the reaction and the need for alternative mechanisms would not have been realized.

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