

A comparative study of the thermal reactivities of some transition metal oxalates in selected atmospheres

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Abstract

A comparative investigation has been made of the nonisothermal, solid-state thermal decompositions of the oxalates of six divalent transition metals (cations: manganese, iron, cobalt, nickel, copper and zinc) in alternative flowing atmospheres, inert (N₂, CO₂), reducing (H₂) and oxidizing (air). Derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC) response peak maxima, providing a measure of reaction temperatures, have been used to determine salt reactivities and thus to characterize the factors that control the relative stabilities of this set of chemically related reactants. Two trends were identified. Trend (1): in the inert and reducing atmospheres, the decomposition temperature (salt stability) increased with rise in enthalpy of formation of the divalent transition metal oxide, MO. It is concluded that the rupture of the cation-oxygen (oxalate) bond is the parameter that determines the stability of salts within this set. Trend (2): the diminution of decomposition temperatures from values for reactions in inert/reducing atmosphere to those for reactions in an oxidizing atmosphere increased with the difference in formation enthalpy between MO and the other participating oxide (MO_{3/2} or MO_{1/2}). The change of cation valence tended to promote reaction, most decompositions in O₂ occurred at lower temperatures, but the magnitude of the effect varied considerably within this set of reactants. Observed variations in stoichiometric and kinetic characteristics with reaction conditions are discussed, together with the mechanisms of thermal decompositions of these solid oxalates.

This approach to the elucidation of crystallization reaction mechanisms emphasizes the value of comparative investigations within the group of chemically related reactants. Previous isothermal kinetic studies had been made for each of the reactants selected here. From these, much has been learned about the form of the (isothermal) solid-state yield–time curves, often interpreted to provide information about the geometry of interface development for the individual rate processes. However, identification of the controls of reactivity, reaction initiation (nucleation) and advance (nucleus growth), is much more difficult to characterize and less progress has been made towards elucidation of the interface chemistry. The trends of reactivity changes with salt compositions, identified here, offer a complementary approach to that provided by the study of single salts. Much of the recent literature on thermal decompositions of solids has been concerned with individual reactants, but many results and conclusions are not presented in the widest possible perspective. Comparisons between systematically related reactants are identified here as providing a chemical context for the elucidation of the chemical steps that participate in interface reactions. The article advocates the use of a more chemical approach in investigations of crystallization (solid-state chemical) reactions.

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1. Introduction

By focussing interest on the relative thermal reactivities of a series of transition metal oxalates, this study is primarily concerned with the chemical properties, including the mechanisms, of a set of selected crystallization reactions [1,2]. Many

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recent reports, concerned with solid-state thermal decompositions, have tended to be preoccupied with mathematical aspects of kinetic analyses, in particular with the calculation of activation energies, E , many examples are given in [3]. This trend appears to have been accompanied by a marked diminution in interest in the chemical characteristics of such rate processes and, somewhat surprisingly, also in the significances of those magnitudes of E which have been reported for numerous reactions. We note that many studies have been directed towards the development of novel calculation routines for the kinetic analysis of reaction rate measurements. A purpose of this paper is to emphasize the importance of the chemical processes involved in a group of such reactions. The present work was undertaken to characterize the reactivities and controls applicable within a set of selected related rate processes, involving relatively simple reactions of known stoichiometry [4–6].

Thermal decompositions of solids, crystallization reactions, are chemical changes and, in principle, behaviour patterns should be capable of being reconciled with the characteristic chemical properties of the reactant constituents. This aspiration has not, however, always been achieved [2,3,6]. Transition metal oxalates were selected for this comparative study because the reactions are relatively simple, the reactants are readily prepared and many have already been studied [2,4,6]. The extension of a recently published study [5] of the relative abilities of various metal oxides, containing the same cations as the oxalates studied here, to promote the decomposition of potassium oxalate, provided one motivation for the present program. A second reason was that alternative controlling processes and chemical steps have been proposed by different researchers to provide mechanistic explanations for metal oxalate breakdown reactions [4,6]. The present report is intended to contribute towards resolution of some of these outstanding problems, by understanding the chemistry of these reactions in greater detail.

Although there have been numerous studies of the solid-state decompositions of diverse metal carboxylates [2,4,6], little is known for certain about the factors that determine their relative and absolute stabilities. The controlling bond rupture step(s) in oxalate anion breakdowns have not been reliably identified. However, thermodynamic considerations have enabled the principal products to be predicted. CO and/or CO₂ are the usual gaseous products and the residue may be the metal, oxide or carbonate, depending on the electronegativity of the constituent cation. It is also shown in the present study, for widely used reaction conditions, that mixtures of solid products may be given, including cation valencies that differ from those in the original reactant. Different kinetic studies of the same reactant have led to the identification of different mechanistic conclusions and different stability controls, including alternative possible ‘rate limiting’ process, some of which are mentioned below. As explained in [6], various literature reports have concluded that the initial step in anion breakdown may be the rupture or rearrangement

of each one of the three dominant bonds in the carboxylate structure, R–CO–O–M. Clearly, further work is required to resolve these inconsistencies.

To contribute towards the resolution of these problems, we report here comparative studies of the thermal decompositions of the transition metal oxalate series, manganese to zinc, in different atmospheres: N₂ (inert), CO₂ (inert/product), H₂ (reducing) and air (oxidizing). An early study [7], concerned with four of these salts (Fe, Co, Ni and Cu), concluded that oxide was the initial product and this was reduced to the metal by carbon monoxide. Dollimore and Griffiths [4] (see also [8]) reported DTA studies of the thermal reactions of 25 metal oxalates in N₂ and in O₂. For the divalent oxalates of Mn, Fe, Co and Ni, Macklen [9] showed that the decomposition temperatures (DTA) in N₂ were in the sequence of decreasing cation electronegativities. The temperatures of these reactions in air, an oxidizing atmosphere, diminished in the sequence of ease of cation oxidation, M²⁺ → M³⁺.

Boldyrev et al. [10] have concluded that the rupture of the C–C link within the oxalate anion is the first step in the thermal breakdown of all oxalates. This bond is regarded as the weakest, supported by observations in [11]. The same model has recently [12] been used to introduce a particularly comprehensive discussion of the thermal decomposition of silver oxalate.

Acheson and Galwey [13] and later Galwey and Mohamed [14] identified the energy barrier to the vacuum thermal decompositions of oxalates as the strength of the cation to oxalate–oxygen bond. For the Ni, Ag, Hg, Mn and Pb oxalates, L’vov concluded [15] that the first step in reactant breakdown is a dissociative evaporation step, with simultaneous condensation of the products of low volatility. The primary volatile products from decompositions of the oxalates containing the first three cations mentioned were identified as CO + CO₂ + $\frac{1}{2}$ O₂ (or O) and for Mn and Pb were 2CO + $\frac{1}{2}$ O₂.

2. Experimental

2.1. Materials

All chemicals used throughout the present study were of Analytical Grade: sodium oxalate and oxalic acid (BDH, England); CoCl₂·6H₂O and MnCl₂·4H₂O (Koch-Light Laboratories, England); CuCO₃·Cu(OH)₂ (Prolabo, France); ZnCO₃ (Hopkin & Williams, England) and NiCl₂·6H₂O (May & Baker, England).

2.2. Preparations of the reactant metal oxalates

2.2.1. Manganese(II) oxalate

9.9 g MnCl₂·4H₂O (0.05 M) dissolved in 250 ml distilled water was slowly added with continuous stirring to 6.7 g

sodium oxalate (0.05 M) dissolved in 250 ml distilled water. The reaction mixture was maintained at 60 °C for 2 h. The precipitated product was filtered, washed several times with distilled water and finally dried at 100 °C.

2.2.2. Ferrous oxalate

The Prolabo product, the dihydrate, was used as received without further purification.

2.2.3. Cobalt oxalate

5.95 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.025 M) dissolved in 250 ml distilled water was added with continuous stirring to 3.35 g of sodium oxalate (0.025 M). The procedures were identical with those used in the preparation of manganese oxalate.

2.2.4. Nickel oxalate

The preparation of nickel oxalate was similar to that for the cobalt and manganese salts, through the addition of an aqueous solution of 5.95 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 250 ml distilled water to an aqueous solution of 3.35 g sodium oxalate in 250 ml distilled water.

2.2.5. Copper(II) oxalate

10.5 g basic copper carbonate (approximate composition, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) was added in small amounts with continuous stirring to 12.6 g oxalic acid in 250 ml distilled water at 60 °C [16]. The blue product precipitated was filtered, washed several times with distilled water and dried at 100 °C.

2.2.6. Zinc oxalate

Zinc oxalate was prepared by the slow addition of 6.27 g (0.05 M) ZnCO_3 , with continuous stirring, to 6.3 g (0.05 M) oxalic acid dissolved in 250 ml distilled water maintained at 60 °C. Stirring was continued for a further 2 h. The white precipitate was filtered, washed several times with distilled water and dried at 100 °C.

2.3. Elemental analysis

The carbon and hydrogen contents of all reactants were determined using standard combustion techniques. The metal content (i.e., Mn, Fe, Co, Ni, Cu and Zn) of each salt was determined using the inductively coupled plasma method (ICP) with a model OES ARL instrument, Switzerland.

2.4. Experimental techniques

2.4.1. Thermal analysis

Thermal analysis measurements (thermogravimetry (TGA), derivative thermogravimetry (DTG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC)) were carried out by a Shimadzu “Stand Alone” thermal analyzer (TGA-50H, DTA-50 and DSC-50, Japan). This was equipped with a data acquisition and handling system (model TA-50WSI, Japan).

Thermal analysis experiments were performed in a dynamic atmosphere (flow rate 40 ml/min) of dry N_2 , H_2 , CO_2 or air. Variations of sample mass and particle sizes are known [17] to have significant effects on the thermal analysis responses (peak shape and maximum peak temperature). Therefore, constant masses (10–15 mg) of gently crushed reactant samples were always used. Each thermal analysis experiment was repeated three times and all mass loss values reported were the average of three measurements: reproducibility was better than $\pm 1\%$. Peak temperatures from DTA and DSC response curves were similarly recorded and were reproducible within $\pm 1^\circ\text{C}$. Highly sintered $\alpha\text{-Al}_2\text{O}_3$ powder (Shimadzu) was used as the reference material in DTA and DSC experiments. Calibrations of the DTA and the DSC instruments for temperature and enthalpy measurements at heating rates between 2 and 30 °C/min were carried out using Specpure indium and zinc metals, Johnson Matthey: melting points 156.6 and 419.5 °C, ΔH , 28.24 and 101.50 Jg^{-1} , respectively [18]. All gases used in the present work (i.e., N_2 , H_2 , CO_2 and air) were 99.0% pure products from the Egyptian Company of Industrial Gases (Nasr City, Egypt).

2.4.2. X-ray diffraction

X-ray powder diffraction analysis of the metal oxalates and of the decomposition products from reactions in each of the atmospheres, and at different temperatures, used a model D5000 Siemens diffractometer (Germany) with Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). An on-line data acquisition and handling system permitted an automatic JCPDS library search [19] and match (Diffrac AT software, Siemens) for phase identification.

2.4.3. IR spectroscopy

Infrared spectra of the reactants, samples partially decomposed at selected temperatures (under different dynamic atmospheres) and the residual solid products were carried out adopting the KBr disk technique using a Magna-FTIR 560 (USA) instrument operated by Nicolet Omnic software.

2.4.4. Enthalpy determinations

Enthalpy (ΔH) measurements for the decomposition processes (and dehydrations of the hydrated salts) were obtained from the DSC response traces at different heating rates and in the different flowing gases.

3. Results and discussion

3.1. Elemental analysis

Elemental analyses of the reactants showed that the manganese, copper and zinc oxalates were prepared in the anhydrous form and the other three salts, ferrous, cobalt and nickel oxalates, were the dihydrates. Analytical data are

recorded below with the theoretically calculated values in parenthesis:

MnC ₂ O ₄	Mn, 37.95 (38.44%) and C, 16.33 (16.79%).
FeC ₂ O ₄ ·2H ₂ O	Fe, 30.71 (31.05%); C, 12.98 (13.34%) and H, 2.41 (2.22%).
CoC ₂ O ₄ ·2H ₂ O	Co, 31.51 (32.39%); C, 12.87 (13.19%) and H, 2.01 (2.20%).
NiC ₂ O ₄ ·2H ₂ O	Ni, 31.74 (32.13%); C, 13.40 (13.13%) and H, 1.92 (2.19%).
CuC ₂ O ₄	Cu, 41.38 (41.93%) and C, 15.42 (15.84%).
ZnC ₂ O ₄	Zn, 42.11 (42.62%) and C, 15.41 (15.65%).

X-ray diffraction observations for the reactants provided confirmation of these elemental analyses. The diffraction patterns obtained gave good matches with the corresponding standard JCPDS data references [19]: MnC₂O₄ (32-0646); FeC₂O₄·2H₂O (22-0635); CoC₂O₄·2H₂O (25-0250); NiC₂O₄·2H₂O (14-0742); CuC₂O₄ (21-0297) and ZnC₂O₄ (37-0718).

3.2. Thermal analysis

Quantitative measurements for each reactant studied are individually presented in Fig. 1a–f, TGA and Fig. 2a–f, DSC response traces for decompositions of the six reactants in the four atmospheres used, N₂, CO₂, H₂ and air. The significant results obtained are tabulated (Table 1), total mass losses and DTG peak maxima (Table 2), DSC peak maxima (Table 3), decomposition enthalpies, ΔH and (Table 4), XRD identification of the residual solid products [19].

3.2.1. Manganese oxalate

Observations and results are summarized in Figs. 1a and 2a and Tables 1–4.

3.2.1.1. In nitrogen. On heating at 5 °C min⁻¹, a large broad (315–415 °C) DTG composite peak was detected, including two maxima at 337 and 389 °C, extensive overlap resulted in no perceptible minimum. The total mass loss, 47.4%, corresponded with expectation for a mixture of products, MnO and Mn₂O₃. On heating at 10 °C, the first peak was almost eliminated, appearing only as an early distortion in the single dominant response at 418 °C (360–450 °C). Here the mass loss, 50.2%, was in accordance with the formation of MnO. After completion of reaction there was a small rise in product mass, attributable to oxidation by trace amounts of oxygen in the flowing nitrogen.

3.2.1.2. In carbon dioxide. On heating at 10 °C min⁻¹, a small DTG response at about 356 °C overlapped extensively with the dominant peak at 425 °C (352–453 °C). The mass loss, 50.4% was in accordance with expectation for the formation of MnO. At 5 °C min⁻¹ the mass loss was 49.5% and DTG peaks were at 350 and 408 °C.

3.2.1.3. In hydrogen. On heating at 5 °C min⁻¹, a large DTG peak maximum occurred at 397 °C (350–420 °C) (at 10 °C min⁻¹ values were 409 °C (365–438 °C)). A small initial response was detected at 341 (and 350 °C). Mass loss values, 50.9% (and 51.0%) were close to, or slightly greater than, expectation for product MnO.

3.2.1.4. In air. On heating at 5 °C min⁻¹, decomposition was completed in a single rate process at relatively lower temperature, DTG peak at 290 °C (275–325 °C). At 10 °C min⁻¹, the response, 299 °C, was completed within a much diminished temperature interval, 287–307 °C. Mass losses, 44.1 and 46.4% on heating at 5 and 10 °C min⁻¹, respectively, were in accordance with expectation for the formation of product mixtures containing both Mn₃O₄ and Mn₂O₃.

3.2.1.5. DTA measurements. The reaction in air (oxygen) was exothermic, expected if the initial CO gas and the residual MnO products were both subsequently oxidized. The reaction in nitrogen was endothermic, consistent with formation of the lower oxidation states of the same products.

3.2.1.6. DSC measurements. Manganese oxalate decompositions in N₂ (414 °C), CO₂ (425 °C) and H₂ (407 °C) atmospheres were endothermic with DSC peak temperature maxima (listed in Table 2) close to the corresponding DTG values. In contrast, the reaction in air (321 °C) was exothermic.

3.2.1.7. Discussion. It has been shown [20] (see also [21,22]) that manganese oxalate decomposition in oxygen proceeds in a lower temperature interval (227–317 °C) than the vacuum reaction (343–363 °C). This was ascribed to the active role of the Mn³⁺ ion in promoting oxalate anion breakdown. Evidence was provided [20] that, in vacuum, a small excess of CO was formed in the early stages of reaction, believed to be accompanied by the formation of an appropriate amount of Mn³⁺. In oxygen, cation (and CO) oxidation is expected.

The above results confirm the significant role of oxygen in promoting this reaction in air at 290–299 °C, attributable to participation by the oxidized cation, Mn³⁺, and at the higher heating rate completion was particularly rapid. These residual products were (relatively) the most highly oxidized. In

Table 1

Effects of different gas atmospheres on the total mass loss (ML% on completion of reaction) and T_{\max} (from the DTG curves) values for decompositions of the different metal oxalates at a heating rate of $10^\circ\text{C}/\text{min}$

Gas atmosphere (40 ml/min)		Mn(II) oxalate	Fe(II) oxalate	Co(II) oxalate	Ni(II) oxalate	Cu(II) oxalate	Zn(II) oxalate
N ₂	ML%	50.2%	55.4%	55.4%	59.4%	56.9%	48.0%
	T_{\max}	418 °C	201.6 264 351 °C	191.5 316.9 °C	229.1 367.6 °C	299.8 °C	411.8 °C
CO ₂	ML%	50.4%	56.6%	55.5%	60.0%	56.0%	48.0%
	T_{\max}	425 °C	204.7 284 384 411.4 °C	190.4 340.1 °C	236.7 375 392 °C	309.6 °C	421.6 °C
H ₂	ML%	51.0%	69.3%	68.0%	68.1%	59.6%	48.1%
	T_{\max}	409 °C	208.8 258.7 407.3 °C	190.4 359.5 370.7 °C	258.7 348.3 °C	283.5 °C	405.3 °C
Air	ML%	46.4%	55.8%	56.0%	60.3%	54.6%	48.2%
	T_{\max}	299 °C	204.5 231.4 °C	199.2 303.1 °C	270.9 340.1 °C	307.1 °C	406.9 °C

ML%: percentage mass loss on completion of reaction. T_{\max} : DTG peak maxima (°C).

Table 2

DSC peak temperature maxima (°C) for the dehydration and the decomposition of the metal oxalates on heating at $10^\circ\text{C}/\text{min}$ in different gas atmospheres, atmosphere flow rate 40 ml/min

Metal oxalate	Process	T_{\max} in N ₂ atmosphere	T_{\max} in CO ₂ atmosphere	T_{\max} in H ₂ atmosphere	T_{\max} in air atmosphere
Anhyd.	Dehyd.	–	–	–	–
MnC ₂ O ₄	Decompn.	414 (n)	425 (n)	407 (n)	321(x)
FeC ₂ O ₄ ·2H ₂ O	Dehyd.	183 (n)	186 (n)	179 (n)	200 (n)
	Decompn	392 (n), 412 (n)	388 (n), 416 (n)	381 (n), 422 (n)	244 (x)
CoC ₂ O ₄ ·2H ₂ O	Dehyd.	185 (n)	181 (n)	173 (n)	179 (n)
	Decompn	387 (n)	404 (n)	375 (x)	320 (x)
NiC ₂ O ₄ ·2H ₂ O	Dehyd.	223 (n)	230 (n)	214 (n)	227 (n)
	Decompn	340 (n), 357 (n)	375 (n)	351 (x)	353 (x)
Anhyd.	Dehyd.	–	–	–	–
CuC ₂ O ₄	Decompn	296 (x)	299 (x)	304 (x)	318 (x)
Anhyd.	Dehyd.	–	–	–	–
ZnC ₂ O ₄	Decompn	407 (n)	419 (n)	405 (n)	390 (n)

DSC response maxima: (n) endothermic, (x) exothermic.

Table 3

Enthalpy (ΔH) changes on dehydration and on decomposition of some metal oxalates during heating at $10^\circ\text{C}/\text{min}$ in different gas atmospheres flowing at 40 ml/min

Metal oxalate	Atmosphere (units)	Air (kJ/mol)	H ₂ (kJ/mol)	CO ₂ (kJ/mol)	N ₂ (kJ/mol)
Anhyd. MnC ₂ O ₄	Dehyd.	–	–	–	–
	Decomp.	111	30.4	78.8	88.0
FeC ₂ O ₄ ·2H ₂ O	Dehyd.	61.2	35	96.2	94.1
	Decomp.	79.2	41.6	60.5	70.2
CoC ₂ O ₄ ·2H ₂ O	Dehyd.	71.0	32.1	84	83
	Decomp.	78.7	10.9	39.7	40.8
NiC ₂ O ₄ ·2H ₂ O	Dehyd.	73.1	20.0	82.3	87
	Decomp.	70.4	33.6	29.3	32.5
Anhyd. CuC ₂ O ₄	Dehyd.	–	–	–	–
	Decomp.	43.5	21.1	18.0	11.9
Anhyd. ZnC ₂ O ₄	Dehyd.	–	–	–	–
	Decomp.	16.6	25.6	62.0	72.1

Trends of ΔH_{decomp} : In nitrogen and in carbon dioxide: Mn > Zn > Fe > Co > Ni > Cu; in hydrogen: Fe > Ni > Mn > Zn > Cu > Co; in air: Mn > Fe > Co > Ni > Cu > Zn.

hydrogen the peak maxima appeared at significantly higher temperatures, 397–409 °C and the residual oxide was MnO. These conclusions are entirely consistent with the previous work [20]. The formation of MnO from reactions in N₂ and H₂ is confirmed by X-ray diffraction (Table 4). During the reaction in N₂ at 10 °C min⁻¹ the initial response is small (about 10% reaction) whereas on heating at 5 °C min⁻¹ this peak represents about 50% reaction. Product mass increases after reactions in N₂ and CO₂ are consistent with some MnO oxidation by traces of O₂ in these flowing gases.

The following conclusions are reached. (i) The pattern of behaviour is entirely consistent with the previous proposal [20] that Mn³⁺ ions participate in controlling the rate of oxalate ion breakdown. This accounts for the relatively much more rapid reaction in air (oxygen), which diminished the reaction temperature by 110 ± 10 °C. This is somewhat less than the difference found by Macklen [9], 150 °C, at the lower

heating rate, 3 °C min⁻¹. (ii) In O₂, the occurrence of smaller DTG peaks at lower temperatures than the dominant reaction in N₂, CO₂ and H₂ may be associated with facilitation of the precursor reaction step required to generate the Mn³⁺ that is an essential participant in manganese oxalate decomposition. This is confirmed in Fig. 3, where the decomposition temperature of the MnC₂O₄/Mn₃O₄ mixture was diminished by about 55 °C, compared with that of the pure salt. (iii) There is strong evidence that a small amount of impurity gas in the reaction atmosphere can exert a perceptible influence on the kinetic characteristics of the overall reaction, accounting for the low temperature peaks during reactions in N₂. This possibility must be remembered in designing rate studies where the small amount of promoter (O₂ yielding Mn³⁺) can have a large kinetic consequence. (iv) The mass gain after completion of decomposition in air is ascribed to oxidation of the lower oxides initially formed.

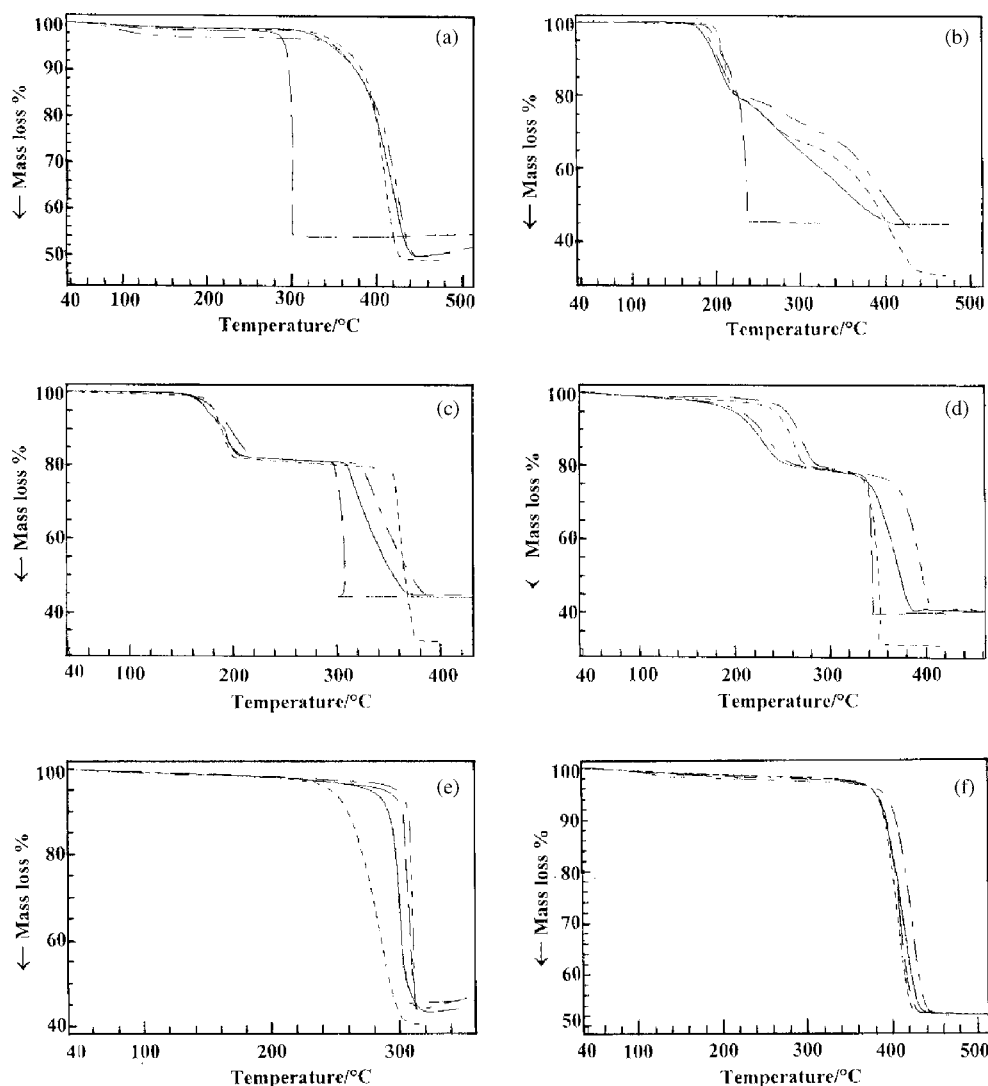


Fig. 1. Thermogravimetric plots of mass losses (%) against temperature (°C) for thermal decompositions, in a flowing, 40 ml/min, atmosphere of N₂, CO₂, H₂ or air, on heating at 10 °C min⁻¹ of: (a) manganese oxalate, (b) ferrous oxalate dihydrate, (c) cobalt oxalate dihydrate, (d) nickel oxalate dihydrate, (e) copper oxalate and (f) zinc oxalate. Atmospheres: N₂, continuous line; H₂, short dashes; CO₂, long dashes; air, alternate long and short dashes.

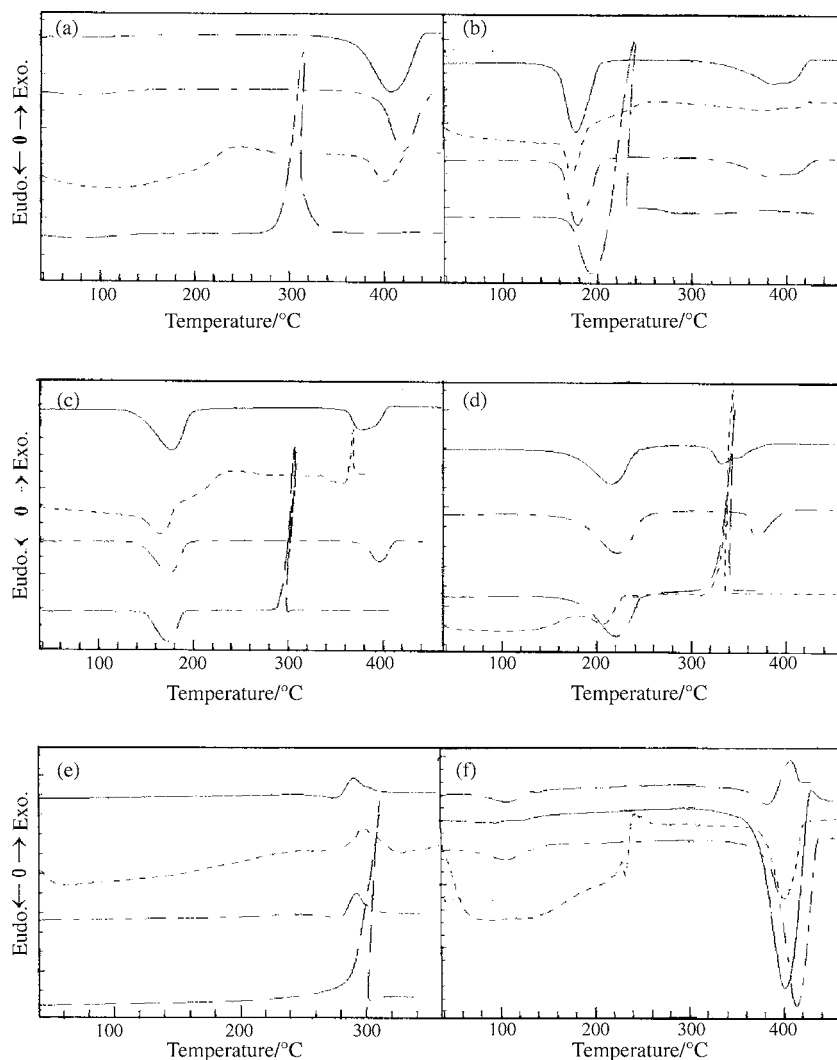


Fig. 2. Differential scanning calorimetric plots of enthalpy output/input (mW) against temperature ($^{\circ}\text{C}$) for thermal decompositions, in a flowing, 40 ml/min, atmosphere of N_2 , CO_2 , H_2 or air, on heating at $10^{\circ}\text{C min}^{-1}$ of: (a) manganese oxalate, (b) ferrous oxalate dihydrate, (c) cobalt oxalate dihydrate, (d) nickel oxalate dihydrate, (e) copper oxalate and (f) zinc oxalate. Atmospheres represented as in Fig. 1.

3.2.2. Ferrous oxalate dihydrate

Observations and results are summarized in Figs. 1b and 2b and Tables 1–4.

3.2.2.1. Dehydration. The first large TG response was ascribed to the precursor dehydration reaction: maxima were between 197 and 207°C for samples heated at $10^{\circ}\text{C min}^{-1}$ (peaks were between 170 and 230°C) and close to 185°C for $5^{\circ}\text{C min}^{-1}$ (160 – 210°C). Mass losses were $19.9 \pm 0.2\%$ which agrees well with expectation (20.0%) for the loss of $2\text{H}_2\text{O}$. It is concluded that dehydration was (largely) completed before the onset of anion breakdown, for reactions in all gases except air, where the contribution from dehydration overlapped with the onset of decomposition and its completion could not be distinguished on the DTG response traces.

3.2.2.2. In nitrogen. On heating in N_2 at $10^{\circ}\text{C min}^{-1}$, this reactant showed two broad and overlapping (235 – 415°C)

DTG response peaks, maxima at 264 and 351°C with an indistinct minimum at 315°C . At the lower rate of heating, $5^{\circ}\text{C min}^{-1}$, a closely similar broad response included maxima at 262 and 334°C . The total mass loss (including dehydration) was 55.4% , close to expectation for the formation of product Fe_2O_3 , 55.6% .

3.2.2.3. In carbon dioxide. Again, on heating at $10^{\circ}\text{C min}^{-1}$, two broad overlapping DTG peaks were found between 240 and 445°C , but the first, 284°C , was relatively smaller (less than half) the dominant peak, maximum 384°C . The mass loss, 56.6% was slightly greater than the reaction in N_2 and is consistent with the formation of a residual mixture containing approximately equal masses of Fe_2O_3 and Fe_3O_4 .

3.2.2.4. In hydrogen. On heating at $5^{\circ}\text{C min}^{-1}$, two DTG peaks were distinguished, maxima close to 255 and 401°C

Table 4

XRD results for identifications of the final solid decomposition products on heating metal oxalates in different gas atmospheres (reaction temperatures shown)

Metal oxalate	In N ₂ atmosphere	In H ₂ atmosphere	In air atmosphere
MnC ₂ O ₄	At 460 °C MnO (maj), card 7-0230 Mn ₂ O ₃ (min), card 24-0508	At 450 °C MnO (maj) MnO ₂ (min), card 12-0141	At 320 °C Mn ₃ O ₄ (maj) Mn ₅ O ₈ (min) MnO ₂ (min)
FeC ₂ O ₄ ·2H ₂ O	At 440 °C Fe ₂ O ₃ (maj), card 15-0615 Fe ₃ O ₄ (min), card 11-0614	At 480 °C Fe (maj), card 6-0696 Fe ₃ O ₄ (min) Fe ₂ O ₃ (min)	At 260 °C Fe ₂ O ₃ (maj) Fe ₃ O ₄ (min) Fe (min)
CoC ₂ O ₄ ·2H ₂ O	At 380 °C Co ₃ O ₄ (maj), card 43-1003 CoO (min), card 9-0402	At 400 °C Co (maj), card 15-0806 Co ₃ O ₄ (min)	At 320 °C Co ₃ O ₄ (maj) Co ₂ O ₃ (min)
NiC ₂ O ₄ ·2H ₂ O	At 400 °C Ni (maj), card 4-0850 NiO (maj), card 22-1189	At 360 °C Ni (only)	At 360 °C NiO (only)
CuC ₂ O ₄	At 350 °C Cu (maj), card 4-0836 CuO (min), card 41-0254 Cu ₂ O (min), card 5-0667	At 350 °C Cu (only)	At 350 °C Cu (maj) CuO (maj) Cu ₂ O (maj)
ZnC ₂ O ₄	At 460 °C ZnO (only), card 36-1451	At 460 °C ZnO (only)	At 460 °C ZnO (only)

maj = major component of residue; min = minor. 'Cards' mentioned refer to [19].

(response ratios about 1:4) for both heating rates, the minimum was close to 300 °C. The first peak represented 10.7% mass loss and the total on completion of decomposition on heating at 10 °C min⁻¹ was 69.3%, close to expectation (68.9%) for the formation of residual Fe metal.

3.2.2.5. *In air*: Decomposition overlapped significantly with the precursor dehydration step on heating at both 5 and 10 °C min⁻¹. After onset of the former there was a sharp

maximum, 220–233 °C, followed by rapid completion of reaction. The total mass change, 55.8% was close to expectation for Fe₂O₃ product, 55.6%.

3.2.2.6. *Discussion*. The first response peaks in Table 1, maxima 202–209 °C, are identified as dehydration (–2H₂O). The predominant mass losses due to decomposition, Fig. 1b, are associated with the peak maxima at 411, 407 and 351 °C for reactions in CO₂, H₂ and N₂, respectively. These occur

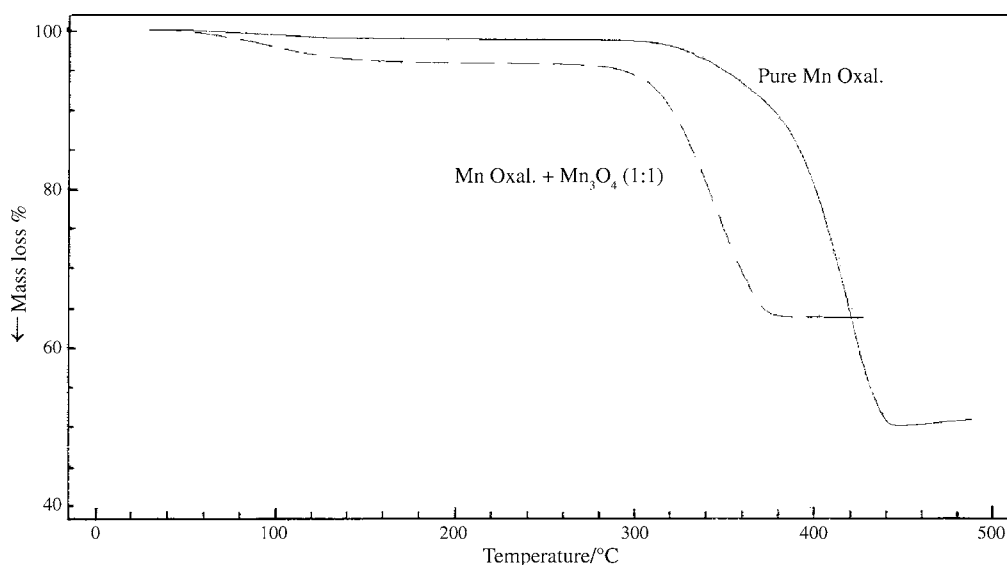


Fig. 3. The decomposition of a manganese oxalate/Mn₃O₄ mixture on heating in N₂ at 10 °C min⁻¹, a plot of mass loss (%) against temperature (°C). The presence of Mn₃O₄ diminishes reaction temperature by about 55 °C.

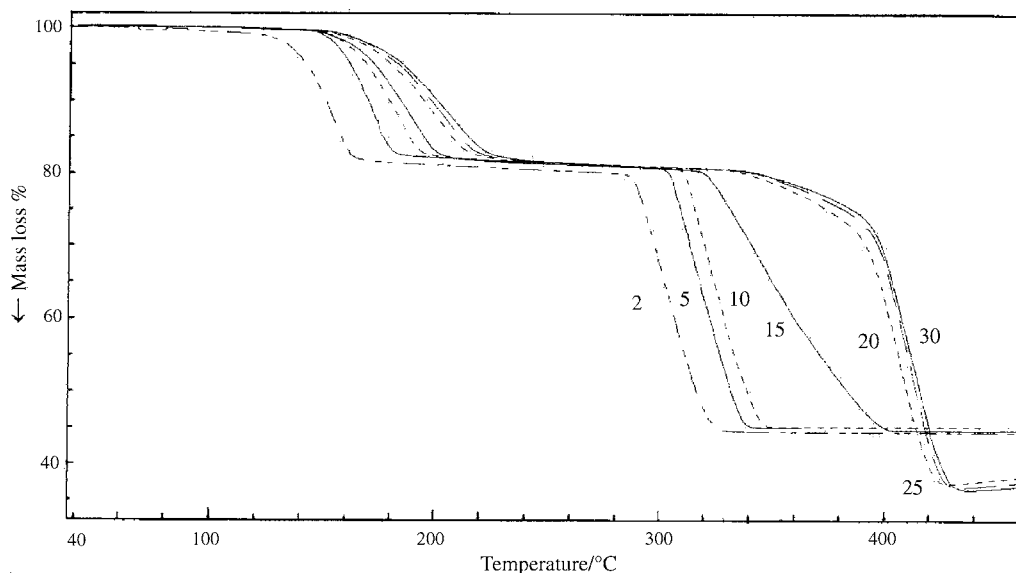


Fig. 4. Plot of mass loss (%) against temperature ($^{\circ}\text{C}$) for the thermal decomposition of cobalt oxalate dihydrate on heating in N_2 at various rates $2\text{--}30\text{ }^{\circ}\text{C min}^{-1}$. Both stoichiometry and reaction rate change with conditions, for discussion see text.

(as expected) at a temperature somewhat above that of the isothermal reaction. The lower temperature of onset of decomposition, Fig. 1b, the peaks at 384 , 259 and $264\text{ }^{\circ}\text{C}$ in CO_2 , H_2 and N_2 , is not consistent with the earlier study [14]. However, the most probable explanation is that a proportion of the Fe^{2+} becomes oxidized during the last stages of dehydration either by disproportionation in water vapour or by O_2 traces in the atmosphere, except for the reactions in H_2 . Promotion of oxalate breakdown by Fe^{3+} accounts for the lower temperature reaction in N_2 . The decomposition of the ferric salt, response maximum at $231\text{ }^{\circ}\text{C}$, Table 1, is rapid at these reaction temperatures [23,24].

A previous study [14] of the isothermal decomposition of ferrous oxalate in vacuum identified the reaction as occurring between 323 and $365\text{ }^{\circ}\text{C}$. The residual products were the mixture ($\text{Fe} + \text{Fe}_3\text{O}_4$) resulting from the disproportionation of unstable FeO . Decomposition of ferric oxalate occurred within a lower temperature interval, $137\text{--}177\text{ }^{\circ}\text{C}$ [23,24]. From isothermal, vacuum decomposition studies it was estimated that the reaction of iron(II) oxalate was completed in about 10 min at $370\text{--}380\text{ }^{\circ}\text{C}$ [14] and for iron(III) oxalate at $180\text{--}185\text{ }^{\circ}\text{C}$ [23]. This difference, about $193\text{ }^{\circ}\text{C}$ agrees well with the value reported by Macklen [9] for the change of reaction temperatures ($192\text{ }^{\circ}\text{C}$), peak maxima, on heating iron(II)

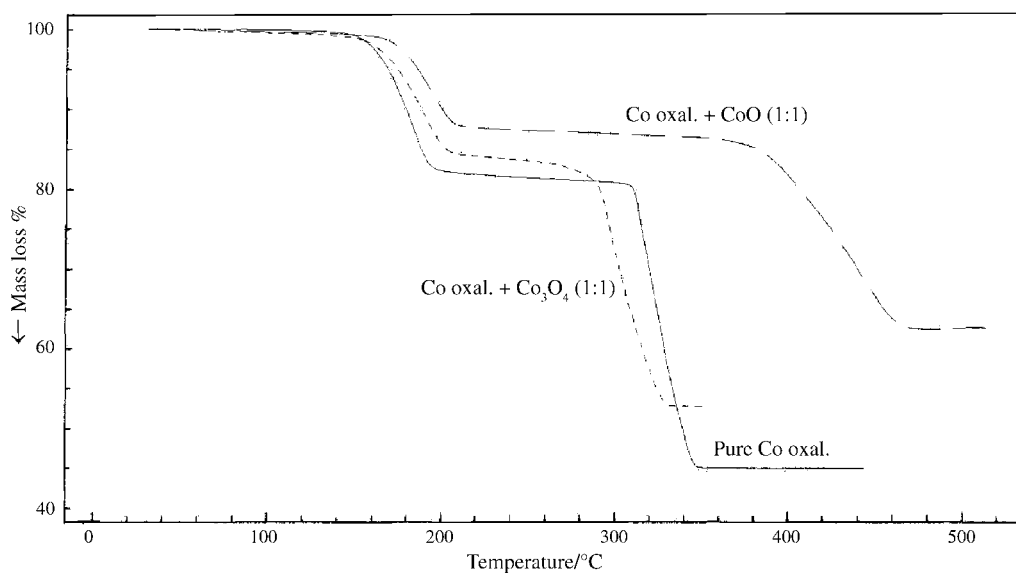


Fig. 5. Plot of mass loss (%) against temperature ($^{\circ}\text{C}$) for the thermal decomposition of cobalt oxalate dihydrate on heating in N_2 at $10\text{ }^{\circ}\text{C min}^{-1}$. The reaction rate is increased by the presence of Co_3O_4 , but diminished by CoO , for discussion: see text.

oxalate in N_2 and in O_2 at $3\text{ }^\circ\text{C min}^{-1}$. The present DTG observations measured the first peaks in N_2 and in H_2 at 264 and $258\text{ }^\circ\text{C}$, respectively, and $219\text{--}232\text{ }^\circ\text{C}$ in O_2 , all somewhat above values expected for decomposition of the iron(III) salt. The second peaks on heating in N_2 , $351\text{ }^\circ\text{C}$, was just below the decomposition of iron(II) oxalate and the higher temperature of reaction in H_2 , $407\text{ }^\circ\text{C}$, is ascribed to reduction of residual oxide to iron metal product. From all the present results, we estimate the peak temperature maximum difference between decompositions in N_2 and O_2 to be $150 \pm 20\text{ }^\circ\text{C}$.

3.2.3. Cobalt oxalate dihydrate

Observations and results are summarized in Figs. 1c and 2c and Tables 1–4.

3.2.3.1. Dehydration. Water evolutions were completed below $220\text{ }^\circ\text{C}$, in a single DTG response that did not overlap with the subsequent decomposition. The measured mass loss was 18.6%, at low heating rates but relatively increased with heating rate, reaching expectation for the dihydrate, 19.7% at $30\text{ }^\circ\text{C min}^{-1}$. It is considered that this small inconsistency does not affect the reactions of current interest.

3.2.3.2. In nitrogen. DTG response peaks were broad and slightly asymmetrical, the onset slope being steeper than the subsequent return to the baseline. Maxima at both heating rates were very close to $317\text{ }^\circ\text{C}$ for responses at $10\text{ }^\circ\text{C min}^{-1}$ ($307\text{--}372\text{ }^\circ\text{C}$) and $5\text{ }^\circ\text{C min}^{-1}$ ($295\text{--}345\text{ }^\circ\text{C}$). Mass losses, 55.4% were slightly greater than expectation for Co_2O_3 formation (54.7%), evidence for the presence of Co_3O_4 (56.12%) in the residue.

Further comparative studies were made of the decomposition in N_2 at various heating rates (Fig. 4). Reactions at 2, 5 and $10\text{ }^\circ\text{C min}^{-1}$ were rapidly completed between 290 and $345\text{ }^\circ\text{C}$, mass losses were close to 55.4% (Co_2O_3 with some Co_3O_4). Heating at 20, 25 and $30\text{ }^\circ\text{C min}^{-1}$ gave responses close to a single line, which included a relatively slow reaction $340\text{--}400\text{ }^\circ\text{C}$ resulting in about 17% mass loss. This was followed by a more rapid decomposition completed at about $430\text{ }^\circ\text{C}$. The total mass losses of 63.0–63.7%, identify the products as a mixture of comparable amounts of CoO and cobalt metal. Intermediate behaviour was found for heating at $15\text{ }^\circ\text{C min}^{-1}$.

Further experiments in N_2 gas, Fig. 5, showed that the addition of Co_3O_4 slightly decreased ($-20\text{ }^\circ\text{C}$) the temperature of onset of cobalt oxalate decomposition and reaction was completed at about $330\text{ }^\circ\text{C}$, comparable with reactions at the lower heating rates. The addition of CoO increased the decomposition temperature, reaction proceeded more slowly in a higher temperature interval and was only completed at about $470\text{ }^\circ\text{C}$.

3.2.3.3. In carbon dioxide. The DTG peak, maximum $340\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C min}^{-1}$, was unsymmetrical ($312\text{--}385\text{ }^\circ\text{C}$), again onset was more rapid than the subsequent completion

of reaction. The mass loss, 55.5%, was the same as that in N_2 .

3.2.3.4. In hydrogen. The DTG response ($335\text{--}365\text{ }^\circ\text{C}$) for decomposition on heating at $5\text{ }^\circ\text{C min}^{-1}$ was an overlapping doublet, maxima 344 and $354\text{ }^\circ\text{C}$, separated by a small minimum. At $10\text{ }^\circ\text{C min}^{-1}$, the components peaks were no longer separated, the single maximum $359\text{ }^\circ\text{C}$ was for the first rate process. The total mass loss, 68.0%, identified cobalt metal as the residual product.

3.2.3.5. In air. Reaction was very rapidly completed at both heating rates, 5 and $10\text{ }^\circ\text{C min}^{-1}$, and DTG response maxima were detected at 294 and $303\text{ }^\circ\text{C}$. The mass loss, 56.0% is close to expectation (56.1%) for the formation of product Co_3O_4 .

3.2.3.6. Discussion. The rate and the products of decomposition in N_2 vary with heating rate (Fig. 4). At heating rates below about $10\text{ }^\circ\text{C min}^{-1}$, reaction was completed by about $345\text{ }^\circ\text{C}$ and the mass losses identify the products as being predominantly Co_3O_4 and Co_2O_3 . In contrast, at the higher heating rates an initially relatively slow reaction rate subsequently increased to yield residual products containing CoO and cobalt metal. This pattern of behaviour is consistent with enhanced reduction of initial product oxides, at the higher heating rates, during temporarily high concentrations of CO within the reactant mass. Separate experiments, Fig. 5, showed that Co_3O_4 significantly promoted cobalt oxalate decomposition whereas CoO significantly decreased the rate. This pattern of conditions-sensitive behaviour is consistent with previous work by Broadbent et al. [25] who found that the kinetics of cobalt oxalate breakdown, $298\text{--}320\text{ }^\circ\text{C}$, were influenced by the temperature of the precursor dehydration step.

At the lower rates of heating, decomposition occurred between 305 and $325\text{ }^\circ\text{C}$, yielding Co_2O_3 and Co_3O_4 , whereas on rapid heating reaction yielded metal in the product from a reaction at up to $410\text{ }^\circ\text{C}$. From the above data, it is estimated that oxygen reduces the reaction temperature by about $40 \pm 10\text{ }^\circ\text{C}$, which is appreciably less than the value $110\text{ }^\circ\text{C}$, in [9].

3.2.4. Nickel oxalate dihydrate

Observations and results are summarized in Figs. 1d and 2d and Tables 1–4.

3.2.4.1. Dehydration. The first DTG response peak ($180\text{--}270\text{ }^\circ\text{C}$), maxima $230\text{--}260\text{ }^\circ\text{C}$, was identified as dehydration and was always completed prior to the onset of decomposition. Mass losses measured, 20.4–20.6%, were slightly greater than expectation for the loss of $2\text{H}_2\text{O}$ (19.7%), presumably due to a small water excess retained on drying.

3.2.4.2. In nitrogen. A single DTG response (330–420 °C), broad and slightly asymmetric, gave maxima between 365 and 370 °C at both heating rates, 5 and 10 °C min⁻¹. Overall mass losses, were consistent with formation of a product mixture containing both Ni metal and NiO. At low heating rates, 2, 5 and 10 °C min⁻¹, the mass losses, 59.4%, agreed with expectation for product NiO (59.1%) and at higher heating rates, 15, 20, 25 and 30 °C min⁻¹, the product contained as much as 50% Ni metal. The peak maximum increased with heating rate between 330 and 390 °C.

3.2.4.3. In carbon dioxide. The DTG peak maximum temperature, 392 °C, was slightly higher than that in N₂ and the mass loss (60.0%) indicated NiO product.

3.2.4.4. In hydrogen. Decomposition occurred with peak maxima at 327–350 °C and within a comparatively narrow temperature interval, 20–25 °C. The mass loss indicated that Ni metal was the only product.

3.2.4.5. In air. At both heating rates, 5 and 10 °C min⁻¹, reaction was completed within a relatively narrow temperature interval (20–25 °C) and DTG peak maxima were similar to those measured in H₂, 330–340 °C. Residual masses were in accordance with the formation of product NiO only.

3.2.4.6. Discussion. There have been many previous studies of the thermal decomposition of nickel oxalate [2,6,26,27] under a variety of conditions and the residual products have been alternatively identified as Ni metal, NiO and their mixtures, as reported above. The present results show that reactions under oxidizing conditions (in air, 330–340 °C) and under reducing conditions (H₂, 327–350 °C) proceed within similar, and relatively narrow, temperature intervals. Decompositions in inert atmospheres occurred at slightly higher temperatures, 365–370 °C peak maxima, and reaction in CO₂ was even greater, 392 °C. These slight diminutions in reactivity may be ascribed to some contribution, or participation, by the volatile products in the controlling breakdown step within the active reaction interface. CO₂ and/or CO formed and temporarily retained in the vicinity of the reaction contact (nickel oxalate)/(Ni and/or NiO) is regarded as apparently influencing interfacial activity and thereby reducing slightly the overall rate of salt decomposition.

The significant conclusion is that the rates of nickel oxalate decomposition are closely similar, whether the metal and/or its oxide is the residual product. This is entirely consistent with previous comparative studies [28] of the thermal reactions of some nickel carboxylates (these did not include the oxalate) in vacuum and in O₂. It was concluded that reactions proceeded as interface processes and isothermal kinetic characteristics were similar, even identical, for each salt, during reactions in vacuum and in O₂. Although Arrhenius parameters showed some variations with the presence or absence of oxygen, the absolute reactivity of each reactant was influenced only slightly by O₂ and/or whether the residual

product was Ni or NiO. From the present observations, it is concluded that the promoting influence of O₂ (presumably through cation oxidation, as with the other cations discussed above) is relatively small, diminishing the reaction temperature by only 10–20 °C.

3.2.5. Copper(II) oxalate

Observations and results are summarized in Figs. 1e and 2e and Tables 1–4.

3.2.5.1. In nitrogen. On heating at 5 °C min⁻¹ a large, relatively sharp (290–305 °C) peak was detected, maximum 296 °C. The mass loss, 55.5%, indicated the formation of some copper metal (expectation 58.1%), but containing significant amounts of the lower oxide (losses to form Cu₂O and CuO were 52.8 and 47.5%, respectively). The response for heating at 10 °C min⁻¹ was closely similar (maximum 300 °C) and the residue (56.9%) contained a higher proportion of metal. Under both conditions, a slow mass increase after completion of decomposition is ascribed to oxidation by impurity O₂ in the flowing atmosphere.

3.2.5.2. In carbon dioxide. On heating at 5 °C min⁻¹, a single sharp peak (300–318.5 °C) was detected with maximum at 310 °C and mass loss 56.0%. This reaction was very similar to that in N₂.

3.2.5.3. In hydrogen. Reactions at 5 and 10 °C min⁻¹ gave relatively broad response peaks between, approximately, 225 and 300 °C, maxima at 270 and 283.5 °C, respectively. Mass losses confirmed expectation that Cu metal was the only residual product.

3.2.5.4. In air. The maxima of the very sharp response peaks on heating at 5 and 10 °C min⁻¹ were at 296.5 and 307 °C, respectively. The mass loss at the higher rate of heating, 54.6%, approached that expected for Cu₂O formation whereas at the lower rate indicated the almost exclusive formation of metal.

3.2.5.5. Discussion. In a previous study [16], it was demonstrated that copper(II) oxalate decomposed through stepwise cation reduction, Cu²⁺ → Cu⁺ → Cu⁰. This mechanism has subsequently been identified in the thermal breakdowns of copper(II) formate and other copper(II) salts of organic acids, see [16,29] and references therein. In copper(II) oxalate decomposition, 242–277 °C, the two consecutive reactions overlapped to a greater extent than in the other related reactants, to give a sigmoid-shaped isothermal yield–time curve. Evidence for this two-step process [16] was obtained from the kinetic analysis, which did not fit the usual solid-state reaction rate models [2] and from analytical measurements. Similarly, the present observations do not distinguish individual contributions from two-rate processes.

Decomposition in vacuum yielded copper metal as the sole residual product [16]. Under the present reaction conditions, except in H₂ where oxidation was not possible, the

mass losses gave evidence that appreciable proportions of the oxides were retained in the products, attributable to O₂ impurity in the atmospheres. The influence of O₂ on the rate of this reaction was small, this reactant had not been considered in [9].

3.2.6. Zinc oxalate

Observations and results are summarized in Figs. 1f and 2f and Tables 1–4.

3.2.6.1. In nitrogen, hydrogen and air. The TG response peak temperatures for decomposition on heating at both 5 and 10 °C min⁻¹ in these three atmospheres were identical, within experimental error: a single peak 385–425 °C, maxima near to 397 and 407 °C, respectively, were detected. Mass losses were close to 48.0%, which is about 1% greater than expectation for the formation of ZnO (47.0%), evidence of a small amount of dissociative sublimation on heating.

3.2.6.2. In carbon dioxide. On heating at 10 °C min⁻¹, the single peak was observed at about 10 °C higher. Presumably CO₂, adsorbed onto the product ZnO, slightly opposes anion breakdown, which is unexpected because ZnCO₃ is known to decompose at a significantly lower temperature, CO₂ is lost at 300 °C [30].

3.2.6.3. Discussion. Apart from the small influence of CO₂, the decomposition of zinc oxalate was independent of the presence of these gases. Reaction temperature is consistent with previous studies [31,32] in which reaction yielded ZnO without the intervention of the carbonate. The present observations detected no perceptible influence of O₂ on zinc oxalate decomposition, a reaction not studied in [9].

4. Conclusions

4.1. Experimental data and kinetic interpretation

The present comparative investigation of relative reactivities, within this set of chemically related and comparable reactants, is intended to complement the more conventional kinetic methods of elucidating thermal behaviour [2,6]. Studies of this type for the present reactants, undertaken to identify the rate equation and to calculate the Arrhenius parameters, to obtain insights into the reaction controls and mechanisms, have already been completed: representative literature citations are given above. The emphasis throughout has been placed upon the, often older, isothermal kinetic measurements because of perceived uncertainties [3] about some methods and theories widely used in recent interpretations of nonisothermal rate data. Many isothermal kinetic and mechanistic research programs have been directed towards the properties and behaviour of a single, individual salt and usually do not explicitly explore the possibility of trends, similarities or differences across sets of chemically related substances.

Few reports of solid-state decompositions place conclusions in a wider, systematic and chemical, context.

The alternative approach used here, through comparative investigations of reactivity data obtained for a set of related reactants, recalls and develops an earlier method of elucidating mechanisms of solid-state reactions [7,9,10]. Former searches for systematic chemical trends and properties from behaviour variations within sets of comparable reactions appears to have become replaced by a preoccupation with the methods of calculating values of *E*, but without much apparent interest in any chemical significance of the results so obtained [3]. The present comparative study extends the former study [9] to measure variations of reactivity for this set of six reactants that contain divalent transition metal cations occupying consecutive positions in the periodic table. The consequences of selected variations of reaction conditions and the presence of reactive gases were determined. The work was also intended to elucidate chemical aspects of the controls and mechanisms of the thermal reactions for this series of oxalates. Systematic variations of behaviour, elucidating the chemical properties of reactant cations, are expected to contribute to the coherent and ordered advance of the subject.

The thermoanalytical (nonisothermal) responses observed on heating each of the six reactants, in the different atmospheres, have been compared with results from the already reported (isothermal) studies, to characterize the chemical changes and rate processes to which each of the peaks relate. Some of the peak shapes observed differed from expectation, based on previous observations for the same reaction, perhaps due to different experimental conditions. Such variations are of potentially considerable significance in quantitative kinetic studies: peak shape determines the rate equation from which the reaction geometry is deduced [2,6]. For kinetic studies is essential to ensure that the rate data measured refer to rate processes controlled by the slowest reaction, the chemical controlling step. During rate measurements undertaken to elucidate reaction mechanisms, it is important to confirm that reaction rates are not modified by secondary controls, as appears sometimes to have been inadequately recognized [3] in kinetic analyses of thermal data for crystallization reactions. Variations of apparent behaviour with reaction conditions have important implications in the interpretation of kinetic data and caution is always essential when inferring chemical conclusions from a minimum of rate measurements. However, such apparent variations are interpreted differently here because comparisons of these effects between the different reactions are of potential value in identifying the factors that contribute towards determining absolute reactivity and/or reaction mechanisms and controls.

4.2. Mechanisms of metal oxalate decompositions

The pattern of reactivities revealed by this study confirms and extends the trend reported by Macklen [9]. It further provides support for the previous conclusion [13,14] that oxalate stability is determined by the strength of the divalent cation

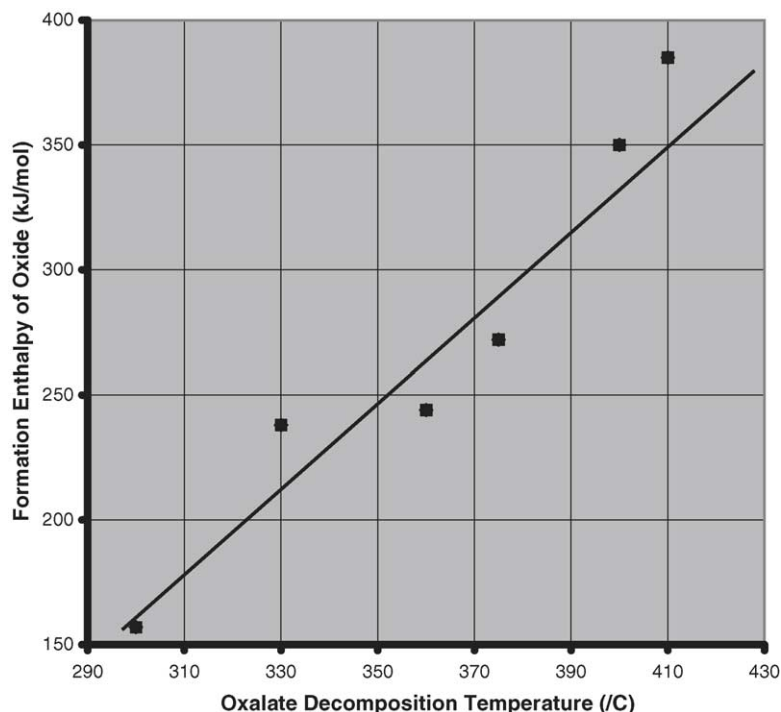


Fig. 6. Trend (1) (see text). Plot of mean reaction temperature, from the present study, for decompositions of the divalent oxalates in inert (N_2 , CO_2) or reducing (H_2) atmospheres against the enthalpy of formation of the divalent oxide, MO. This trend supports the previous conclusion [13,14] that solid-salt stability is determined by the metal to oxalate–oxygen bond strength, $M-OCO \cdot COO \dots$.

bond with the carboxylate anion, $\dots OCO-M-OCO \dots$ as shown in Fig. 6. An approximately linear relationship is found between the mean DTG peak maximum temperatures for (divalent) salt decompositions in an inert atmosphere and the enthalpy of divalent metal oxide formation, MO. The latter parameter is regarded as providing a measure of the cation-to-anion bond strength in the metal oxalate. The trend in both parameters is:



The temperatures of completion of oxalate decompositions vary significantly in the sequence: $Mn(445^\circ C) > Zn(439^\circ C) > Fe(409^\circ C) > Ni(387^\circ C) > Co(370^\circ C) > Cu(320^\circ C)$ (the molten and monovalent potassium oxalate decomposes at a significantly higher temperature, $600^\circ C$ [5]). This systematic variability is regarded as evidence that rupture of the ‘central’ C–C anion bond is not the controlling step in the oxalate decompositions [10–12].

This conclusion also differs from that of Macklen [9] who finds that reaction temperatures decrease with decreasing electronegativity of the metal and concludes that decomposition occurs by rupture of the C–O bond to give the metal oxide. This sequence was not adequately confirmed here. The relatively small changes of electronegativities [33] for Ni (1.91), Cu (1.90) and Co (1.88) do not follow the same sequence as the significant differences of reaction temperatures, given above. For the other salts the electronegativity values show a wider variation, Fe (1.83), Zn (1.65) and Mn (1.55) but again the reaction temperature differences do not

correlate. This trend is regarded as less satisfactory whereas the increase in reaction temperature with MO stability is consistent with decomposition control by M–O bond strength.

4.2.1. Isothermal activation energies

Magnitudes of E reported from isothermal studies of these decompositions do not readily or obviously correlate with the sequence in Trend (1). Representative values of E ($kJ\ mol^{-1}$) from reports of decomposition studies of divalent oxalates include the following: Mn: 141 [2], 180 [22]; Zn: 210 [31], 197 [32]; Fe: 157 [14]; Ni: 210 [26], 160 [27]; Co: (small), 168 [25] and Cu: (about) 200 [34], 180 [16]. No trend is discerned, indeed the scatter of variations between individual values reported by different workers, or even within particular studies of a single reactant [25,34], is comparable with the apparent differences between the different salts. We conclude that magnitudes of E do not provide a measure of absolute reactivity [3], it appears that values are condition-dependent.

Other observations, from the present comparative studies, that identify potential difficulties in the interpretation of nonisothermal TGA kinetic data include the following. The stoichiometries and rate characteristics (the yield–time–temperature curve shape) of the decompositions of cobalt (Fig. 4) and nickel oxalates varied significantly with reaction conditions. This was identified here as a consequence of oxide reduction during those reactions in which a sufficient CO concentration was maintained within the reactant sample. The possible participation of secondary reactions must be considered in thermoanalytical kinetic studies where data

interpretation is sensitive to reaction–response curve shape. It is further noted, for the decompositions of manganese and ferrous oxalates, that the presence of a small quantity of O₂ impurity in the (inert) flowing atmosphere introduces into the reactant a sufficient amount of higher valent cations to cause considerable distortions of the early response peaks. Clearly, the provision of an alternative, preferred reaction path through the formation of an active, but unintended and unrecognized, intermediate (a higher valent cation) may invalidate kinetic and mechanistic conclusions. Both of the effects described here are significant and are potentially capable of influencing apparent kinetic behaviour.

4.2.2. *Chemistries and enthalpies of thermal reactions*

The pattern of reaction enthalpies reported in Table 3 is consistent with the variations of chemical characteristics between these salts. In both inert atmospheres, N₂ and CO₂, ΔH values for decompositions were similar and Trend (1) is found again. A difference is that the (approximately similar) values for the Ni and Co oxalates are here reversed which may be due to different compositions of the product oxides. We also note that the largest enthalpies, and highest reaction temperatures, are associated with the oxide-forming reactions (MnO, ZnO, FeO), lower for Ni and Co, where reaction conditions determine whether oxide or metal is given (Fig. 4) and lowest for the copper salt which yields the metal. Residual products usually contain a proportion of oxide, which may be evidence that MO is the primary decomposition product, subsequently possibly (depending on conditions) reduced by the CO concurrently formed. Enthalpies of reactions in H₂ were generally less, attributable to the formation of CO and usually the lower oxides. The exothermic reactions in air result from the oxidation of CO to CO₂ and the formation of the (sometimes) higher oxides of the residual metals. Enthalpies correlate more satisfactorily with the specific chemical properties of the cations in these salts than with the pattern of isothermal kinetic behaviour.

4.2.3. *The role of oxygen in promoting decompositions of transition metal oxalates*

Decomposition temperatures of the Mn, Fe, Co and Ni salts (those containing oxidizable cations) were significantly diminished by the presence of oxygen. This trend followed the pattern described earlier by Macklen [9], the largest diminutions being found for the most easily oxidized cations. He suggested that the first step in salt breakdown is cation oxidation, $M^{2+} \rightarrow M^{3+}$. It is alternatively possible that the chemical changes proceed at an active (solid-state) reaction interface [2], here a metal oxalate/oxide contact, where oxygen at the oxide surface interacts with the cations and anions of the salt. This is represented as a heterogeneous catalytic-type reaction in which adsorbed oxygen promotes anion breakdown resulting in the formation of CO₂ and metal oxide (whereas retained adsorbed CO would be expected to inhibit activity and possibly reduce the oxide).

Oxygen (reactions in air) considerably promoted the decompositions of Mn and Fe oxalates (Table 1), reaction temperatures were diminished by more than 100 °C. The effect is significantly less for cobalt oxalate, about 40 °C, even lower (15 °C) for nickel oxalate and not detected for copper(II) and zinc oxalates, consistent with the observations reported by Macklin [9]. Results are summarized in Fig. 7, showing Trend (2):



In Fig. 7, a measure of the promotion of decomposition by O₂ (the temperature difference between reaction in an inert atmosphere and that in air) is plotted against the difference of the enthalpies of formation of the divalent oxide and the other oxide participating. For copper, the Cu₂O value was taken and zinc forms only ZnO. More detailed investigations of the mechanisms of these individual reactions are required to identify the rate-controlling parameters. It is possible that the reactions with oxygen may proceed at a heterogeneous reactant–product interface, through the participation of a residual oxide phase at which superficial oxidation occurs. However, hitherto, little information has been obtained concerning the chemical characteristics of such reactions.

From parallels with kinetics and mechanisms discussed for the decompositions of nickel formate [35] and of copper formate [36], there is the possibility that the reactions studied here proceed by heterogeneous catalytic breakdown of the oxalate anion on the product phase, metal and/or oxide. All these reactions have been studied within approximately comparable temperature intervals. Because the factors controlling such surface processes have not yet been reliably or comprehensively characterized, it is premature to attempt to formulate detailed mechanisms of the present reactions. Chemical behaviour, however, appears to be more complicated than has been recognized.

4.2.4. *Comment: isothermal and nonisothermal kinetic studies of the decompositions of divalent transition metal oxalates*

Published kinetic and mechanistic studies of the salts studied here [2,6] have characterized reaction geometries and other aspects of the thermal rate processes for these individual compounds. The forms of the yield–time curves have been correlated with appropriate kinetic models representing solid-state advancing interface reactions. Much less progress has been made towards elucidating interface chemistry and the overall controls of reactivity. Measured values of E have not always been identified with a specific rate controlling step, for each individual salt or within any collective pattern, and chemically significant trends have not been recognized. The present study is intended to complement this approach through these comparative studies of absolute reactivities of chemically related salts, together with the influences of gaseous reactants. This is intended to introduce additional perspectives from which the detailed chemistry of these re-

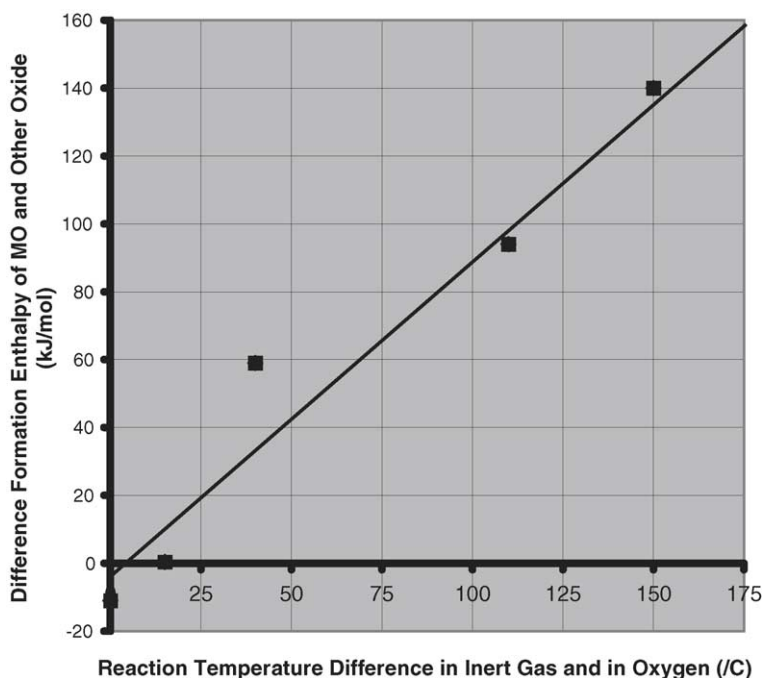
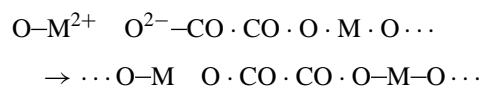


Fig. 7. Trend (2) (see text). Plot of temperature differences between decompositions of divalent oxalates in inert or reducing atmospheres (N_2 , CO_2 , H_2) and those in oxidizing atmospheres against difference of enthalpy of formation of the divalent oxide (MO) and the other metal oxide, $MnO_{3/2}$, $FeO_{3/2}$, $NiO_{3/2}$, $CuO_{1/2}$, and $CoO_{4/3}$. No value for $CoO_{3/2}$ could be found, possibly explaining its relatively greatest distance from the line, no higher oxide of zinc is known.

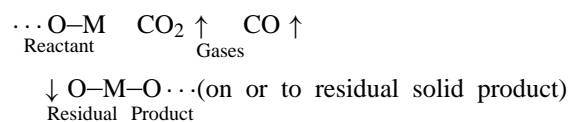
actions may be elucidated in greater detail. Interpretations incorporating complementary types of evidence are more likely to be reliable than conclusions based on limited data.

The observations reported above reveal a pattern of absolute reactivity in which salt decomposition temperature is identified as increasing with the strength of the M–O bond, Trend (1), Fig. 6. It is suggested, therefore, that control is through electron transfer, involving rupture/dissociation of the bond between oxalate–oxygen and the divalent cation. Furthermore, from Trend (2) it is concluded that the availability of more highly oxidized cations, M^{3+} , (during reactions in oxygen) facilitates this electron transfer, thereby diminishing reaction temperature (and again recognizing the importance of electron transfer). This model is represented mechanistically as follows.

The first step is dissociation through electron transfer (facilitated by a cation of higher valency):



This may then revert to the original structure or rearrange through breakdown of the oxalate radical, including rupture at the weakest [12] bond ($\cdots C-C \cdots$):



The temperature of the initial dissociation step is specific to each cation, varies with its oxidation state and may be

followed by breakdown of the link with the anion. Subsequent steps involve rupture of the $\cdots C-C \cdots$ link in the oxalate radical ion (the weakest bond [12]) forming CO_2 and CO , the latter may result in reduction of initial MO product to metal. It is suggested that this sequence of chemical changes takes place at an active interface advancing progressively into each reactant crystallite. No step can be regarded here as a dominant (exclusive) controlling process, the activation energies cited in the text do not correlate with reaction temperatures. The sequence of anion breakdown steps may be similar in all the oxalates and, within the interface, exert some influence (control) on the step identified above as ‘dissociation’.

From the above pattern of behaviour we conclude that chemical trends have been discerned within this set of thermal decompositions involving related reactants. Information not directly obtained from studies of single reactants is thereby provided and is, therefore, to be welcomed as an alternative approach to the elucidation of interface chemistry. This method of comparative studies has been available for decades, e.g. [9], but has become neglected in recent years. It is recommended that the value of such considerations, exploiting the methods of systematic chemistry, should now be reappraised in the search for future advancement in a field where many reports appear as isolated and individual contributions to the literature [3]. Scientific advance implies the development and expansion of coherent and systematic theoretical foundations, trends and aspirations that are not always obvious in many recent reports of solid-state decompositions, crystallization reactions [1,2].

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