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THERMAL DECOMPOSITION OF CARBONATES, CARBOXYLATES, OXALATES, ACETATES, FORMATES, AND HYDROXIDES

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ABSTRACT

A study is reported of the controlled decomposition of various metal carbonates, carboxylates, oxalates, acetates, formates and hydroxides and their common hydrates, carried out in a thermogravimetric analyzer, a differential scanning calorimeter, and a differential thermal analyzer. Various sample sizes, heating rates, and ambient atmospheres were used to demonstrate their influence on the results. Results are given on intermediate compounds, on the temperature range of decomposition for each compound, and on reaction kinetics.

INTRODUCTION

The kinetics of solid dehydrations and decomposition reactions of various carbonates, carboxylates, oxalates, acetates, formates and hydroxides are of wide interest because of applications to calcination in metallurgy [1], to the preparation of high surface area materials for catalysts, molecular sieves and adsorbents [2], and in connection with thermochemical cycles proposed for water splitting [3].

Such rate studies are often run in thermogravimetric analyzers (TG) at relatively high heating rates (10°C min^{-1} or 20°C min^{-1}), but slower rates are needed to avoid endothermic temperature inhomogeneities and possible temperature gradients between a gas phase and a solid reactant. Furthermore, many salt hydrates have stable intermediate hydrates, some of which are completely masked at high heating rates [4]. Kinetic measurements obtained from the same compound can therefore differ widely, making dependable correlation impossible [5] and scale-up more difficult. The inconsistencies in reported values for initial decomposition temperatures of some metal carboxylates were summarized by Duval [6], Dollimore and Nicholson [7], and McAdie and Jervis [8].

In the study reported here a series of 10 metal carbonates, 10 oxalates, eight acetates, and two formates were decomposed in a thermal analysis apparatus with the objectives of (1) revealing any intermediate compounds, (2) determining the stable temperature range of each compound, and (3) measuring the reaction kinetics.

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TABLE 1

Sample compositions. Specification in wt.%.

A. Carbonates

Compound	Source	Assay	Insoluble matter
$MgCO_3 \cdot n\ H_2O$	Baker	42.4 as MgO	0.002 (in HCl)
$ZnCO_3 \cdot Zn(OH)_2$	Baker	71.8 as ZnO	0.10 (in H_2SO_4)
$CuCO_3$	Baker	55.8 as Cu	0.003 (in HCl)
$CdCO_3$	Fisher	99.95 as $CdCO_3$	0.008 (in HCl)
$SrCO_3$	Baker	99.9 as $SrCO_3$	
Ag_2CO_3	Fisher	99.95 as Ag_2CO_3	0.04 (in HNO_3)
$CaCO_3$	Fisher	99.92 as $CaCO_3$	
$MnCO_3$	Baker	43.0 as Mn	0.01 (in HCl)
$NiCO_3$	Baker	40.9 as Ni	0.007 (in HCl)
$CoCO_3$	Coleman and Bell	49.5 as Co	0.4 (in HCl)

B. Acetates and hydroxides

Compound	Source	Assay	Insoluble matter
$Zn(CH_3COO)_2 \cdot 2\ H_2O$	Baker	99.0—101.0	0.005
$Al(OH)(CH_3COO)_2 \cdot H_2O$	Pfaltz and Bauer	99.12	
$Pb(CH_3COO)_2 \cdot 3\ H_2O$	Baker	99.5	0.01
$Ba(CH_3COO)_2$	Baker	99.9	0.005
$Cu(CH_3COO)_2 \cdot H_2O$	Baker	99.7	0.003
$Mg(CH_3COO)_2 \cdot 4\ H_2O$	Baker	100.5	0.003
$Co(CH_3COO)_2 \cdot 4\ H_2O$	Baker	99.7	0.010
$Ca(CH_3COO)_2 \cdot H_2O$	Baker	100.1	
$Ba(OH)_2 \cdot 8\ H_2O$	Baker	99.0	0.01 (in HCl)
$Ca(OH)_2$	Baker	98.0	
$Al(OH)_3$	Baker	100.0	
$Mg(OH)_2$	Mallinckrodt	>95.0	

C. Formates and oxalates

Compound	Source	Assay
$Zn(COOH)_2 \cdot 2\ H_2O$	Pfaltz and Bauer	99.90
$Fe(COOH)_3 \cdot H_2O$	Pfaltz and Bauer	98.7
$ZnC_2O_4 \cdot 2\ H_2O$	Pfaltz and Bauer	99.94
$MnC_2O_4 \cdot 2\ H_2O$	Pfaltz and Bauer	99.89
$CoC_2O_4 \cdot 2\ H_2O$	This research	98.22 on TGA
$NiC_2O_4 \cdot 2\ H_2O$	This research	97.89 on TGA
$MgC_2O_4 \cdot 2\ H_2O$	This research	98.42 on TGA
$FeC_2O_4 \cdot 2\ H_2O$	This research	99.01 on TGA
BaC_2O_4	This research	99.41 on TGA
PbC_2O_4	This research	98.72 on TGA
CuC_2O_4	This research	97.85 on TGA
$CaC_2O_4 \cdot H_2O$	Fisher	Nitrate = 0.005; Fe = 0.01; Heavy metals = 0.025; Sr = 0.02; Mg = 0.02; Na = 0.02; K = 0.02

Chloride	Sulfate	Nitrate	Fe	Pb	Others
0.0008	0.002		0.0003	0.0002	Ca = 0.016
0.001	0.005	0.008	0.0005	0.005	
0.0005	0.001	0.030	0.02		
0.0006	0.001	0.01	0.0001	0.002	Cu = 0.0004; Zn = 0.05; alkaline earths = 0.04
0.001	0.002	0.01	0.0005	0.0002	Ba = 0.001
0.002	0.002				
0.0005	0.003		0.0005	0.003	Na = 0.02; Sr = 0.04; Ba = 0.003; Mg = 0.006; K = 0.02; F = 0.0005
0.02	0.005		0.002		Other heavy metals = 0.002; Zn = 0.05
0.001	0.005		0.002	0.001	Cu = 0.003; Co = 0.08; Zn = 0.003
0.01	0.06		0.01		Alkaline earths = 0.75; Cu = 0.06; Ni = 0.5

Chloride	Sulfate	Pb	Fe	Other
0.005	0.002	0.002	0.0005	As = 0.00005
0.0005				Cu = 0.002
0.0005	0.13	0.0005	0.0003	Nitrate = 0.01
0.01	0.001		0.001	
0.0008	0.002	0.0002	0.0002	Ba = 0.0005; Ca = 0.010; Mn = 0.0006; K = 0.0006; Na = 0.001; Sr = 0.001
0.0005	0.002	0.001	0.0008	Cu = 0.001; Ni = 0.05; Zn = 0.010
0.0009	0.028	0.0005	0.0002	Other metal sulfates = 0.14
0.001			0.001	Sulfide = 0.001; Ca = 0.05; Sr = 0.8; Heavy metals = 0.0005; $BaCO_3$ = 1.0
0.025	0.05	0.003	0.05	
0.002	0.002	0.0005	0.004	
		0.005		As = 2 ppm; CaO = 0.5

EXPERIMENTAL

Except for the decomposition studies for some of the oxalates, most of the salts needed were obtained from commercial sources. The oxalates of cobalt, nickel, magnesium, iron, lead, barium and copper were synthesized from sulfates or nitrates by precipitating the metal ions with potassium oxalate. The solutions were heated to 70°C with constant agitation. One hour later, the precipitates were filtered and washed on No. 2 filter paper. The same procedure was repeated at least two times, until the TG weight determination agreed with theoretical expectation for the compound being made. The oxalate products were oven dried at 50°C and exposed to air. Hydration was obtained by reaction with humidity in the air. Detailed information on purities and compositions for each compound is given in Table 1.

Each decomposition run was conducted on a Model 990 Dupont Instrument Co. thermogravimetric analyzer with differential scanning calorimeter (DSC) and differential thermal analysis (DTA) modules. Heating rates were varied from 1°C min^{-1} to 20°C min^{-1}. Sample weights were kept between 10 and 20 mg as suggested by previous workers, and nitrogen flow of 80 cm^3 min^{-1} was maintained through the gas space (approximately 64 cm^3) over the sample, to drive off the gas product of reaction. Each of the runs was also repeated in air for each reaction. After the preliminary tests were finished, TG runs for the same materials were conducted at the slower heating rates of 1°C min^{-1} over the temperature ranges of interest, for more accurate determination of the various decomposition temperatures and compositions.

RESULTS AND DISCUSSION

Intermediate compositions

With a few exceptions, most of the compounds studied exhibited one or more, more or less stable intermediate compositions as they decomposed in the TGA. The results are summarized in Table 2 in the form of an extensive list of compositions and corresponding temperatures of initial and final decomposition. A typical TG thermogram is reproduced for reference in Fig. 1.

Heating rates

As is well known [4], TG results are extremely sensitive to heating rates. With this in mind, the tests reported in Table 2 were all run at the very slow rate of 1°C min^{-1}. For additional comparison duplicate tests were made at 5°C min^{-1} or 10°C min^{-1}. As expected, the recorded decompositions were observed to occur at somewhat elevated temperatures, presumably a reflection of the time needed for heat conduction in the various solids. A typical effect of the 5°C min^{-1} rate is to move the maximum rate to a temperature about 20—40°C higher than found at 1°C min^{-1}, and for selected compounds (e.g. BaC_2O_4, NiC_2O_4, FeC_2O_4, $MnCO_3$) the increases were as great as 80—90°C.

TABLE 2

Compositions identified by TG.

Heating rate: 1°C min^{-1}; atmosphere: N_2.

Compound	Temp. (°C)	
	Initial decomp.	Final decomp.
$ZnC_2O_4 \cdot 2\,H_2O$	105	135
ZnC_2O_4	320	380
ZnO	>450	
$MnC_2O_4 \cdot 2\,H_2O$	110	130
MnC_2O_4	275	380
Mn_3O_4	>450	
$CaC_2O_4 \cdot H_2O$	135	165
CaC_2O_4	375	470
$CaCO_3$	>500	
$MgC_2O_4 \cdot 2\,H_2O$	130	250
MgC_2O_4	390	455
MgO	>475	
BaC_2O_4	370	535
$BaCO_3$	>600	
$NiC_2O_4 \cdot 2\,H_2O$	135	260
NiC_2O_4	280	335
Ni	>360 (melted)	
$CoC_2O_4 \cdot 2\,H_2O$	130	200
CoC_2O_4	280	350
Co	>400 (melted)	
CuC_2O_4	175	245
Cu	>300 (melted)	
PbC_2O_4	270	350
Pb	>450 (melted)	
$FeC_2O_4 \cdot 2\,H_2O$	120	185
FeC_2O_4	190	320
Fe	>350 (melted)	
$Ca(CH_3COO)_2 \cdot H_2O$	30	210
$Ca(CH_3COO)_2$	315	490
$CaCO_3$	605	725
CaO	>800	
$Ba(CH_3COO)_2$	412	484
$BaCO_3$	>500	
$Al(OH)(CH_3COO)_2 \cdot H_2O$	30	70
$Al(OH)(CH_3COO)_2$	148	350
Al_2O_3	>600	
$Cu(CH_3COO)_2 \cdot H_2O$	70	125
$Cu(CH_3COO)_2$	180	320
$Cu_2O \cdot CuO$	>350	
$Pb(CH_3COO)_2 \cdot 2\,H_2O$	23	60
$Pb(CH_3COO)_2$	165	290
$PbCO_3$	290	343
PbO	>400	

TABLE 2 (continued)

Compound	Temp. (°C)	
	Initial decomp.	Final decomp.
$Mg(CH_3COO)_2 \cdot 4\ H_2O$	45	125
$Mg(CH_3COO)_2$	310	328
MgO	>600	
$Co(CH_3COO)_2 \cdot 2\ H_2O$	58	104
$Co(CH_3COO)_2$	115	260
$Co(CH_3CO)_2$	260	330
Co_3O_4	>500	
$Zn(CH_3COO)_2 \cdot 2\ H_2O$	60	78
$Zn(CH_3COO)_2$	170 (sublimed)	
$Zn(COOH)_2 \cdot 2\ H_2O$	85	120
$Zn(COOH)_2$	200	300
ZnO	>350	
$Fe(COOH)_3 \cdot H_2O$	70	105
$Fe(COOH)_3$	115	265
Fe_2O_3	>250	
$Ca(OH)_2$	325	415
CaO	>450	
$Mg(OH)_2$	285	380
MgO	>400	
$Al(OH)_3$	210	550
Al_2O_3	>600	
$Zn(OH)_2$	260	350
ZnO	>400	
$Ba(OH)_2 \cdot 6\ H_2O$	24	70
$Ba(OH)_2$	78	94
BaO	>100	
$CdCO_3$	280	375
CdO	>425	
$MnCO_3$	30	380
$2\ MnO \cdot MnO_3$	390	440
Mn_3O_4	>450	
$NiCO_3$	20	350
NiO	>350	
$SrCO_3$	710	945
SrO	>950	
$ZnCO_3$	205	258
ZnO	>280	
$CuCO_3 \cdot Cu(OH)_2$	190	310
CuO	>350	
$2\ CoCO_3 \cdot 3\ Co(OH)_2$	240	320
Co_3O_4	>350	
$4\ MgCO_3 \cdot Mg(OH)_2$	340	430
MgO	>500	

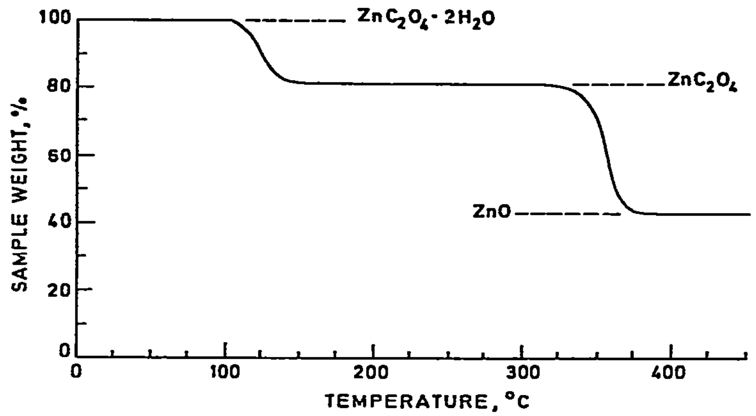

Fig. 1. Thermogravimetric results for zinc oxalate hydrate obtained at a heating rate of 1°C $\min^{-1}$ (20—450°C).

Reaction kinetics

It is not to be expected that any single kinetic expression would be applicable to the wide range of decompositions of this study. Nevertheless, the *n*-th order equation

$$\frac{d\alpha}{dt} = k_0(1-\alpha)^n \exp(-E/RT) \tag{1}$$

is a convenient basis for comparison, since it subsumes most of the prior nucleation and diffusion models [9]. The data from each decomposition run were tested empirically by fitting to the linear form of eqn. (1), and the values of the kinetic parameters were computed by standard procedures, using appropriate statistical evaluations for estimating the confidence intervals of the computed slope and intercept, based on the Student "*t*" distribu-

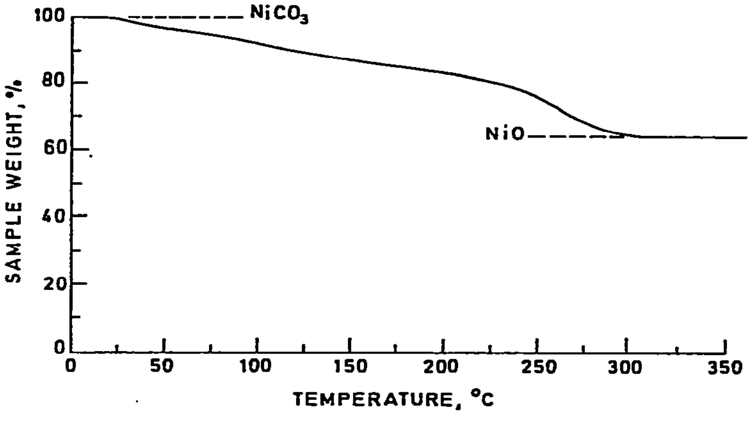

Fig. 2. Thermogravimetric results for nickel carbonate obtained at a heating rate of 1°C $\min^{-1}$ (20—350°C).

TABLE 3

Kinetic parameters for decompositions under nitrogen

Compound		Conversion range for regression fit	Reaction order	Energy of activation (kcal gmole^{-1})	Pre-exponential parameter (sec^{-1})	Standard error (%)
Initial	Final					
$CdCO_3$	CdO	0.03–0.98	2/3	36.0 ± 0.5	6.67×10^{9}	6.2
$CaCO_3$	CaO	0.02–0.98	2/3	73.3 ± 0.6	2.64×10^{13}	6.7
$SrCO_3$	SrO	0.04–0.99	1/2	71.9 ± 0.4	2.09×10^{10}	3.8
$ZnCO_3$	ZnO	0.03–0.99	2	100.0 ± 0.8	4.06×10^{40}	4.2
$CuCO_3 \cdot Cu(OH)_2$	CuO	0.04–0.14	2	19.1 ± 1.0	9.97×10^{3}	5.9
		0.14–0.98	2	84.0 ± 2.3	1.65×10^{30}	7.2
$2\ CoCO_3 \cdot 3\ Co(OH)_3$	$3\ Co_3O_4 \cdot CoO$	0.05–0.95	2	66.3 ± 1.6	9.11×10^{23}	5.6
$4\ MgCO_3 \cdot Mg(OH)_2$	MgO	0.01–0.95	1	58.8 ± 0.3	2.77×10^{16}	2.1
$ZnC_2O_4 \cdot 2\ H_2O$	ZnC_2O_4	0.02–0.99	2/3	37.3 ± 0.3	4.41×10^{17}	6.3
ZnC_2O_4	ZnO	0.01–0.99	1	104.0 ± 0.2	1.81×10^{32}	2.2
$MnC_2O_4 \cdot 2\ H_2O$	MnC_2O_4	0.04–0.97	1	62.5 ± 0.8	1.37×10^{32}	8.1
MnC_2O_4	Mn_3O_4	0.02–0.70	2	29.5 ± 0.5	5.37×10^{7}	4.5
		0.70–0.97	2	61.7 ± 0.6	3.46×10^{19}	5.2
$CaC_2O_4 \cdot H_2O$	CaC_2O_4	0.05–0.96	1/2	37.2 ± 0.1	2.83×10^{16}	1.9
CaC_2O_4	$CaCO_3$	0.05–0.96	2/3	59.4 ± 0.6	1.45×10^{15}	3.5
$MgC_2O_4 \cdot 2\ H_2O$	MgC_2O_4	0.04–0.93	2	50.7 ± 1.4	6.38×10^{21}	4.2
MgC_2O_4	MgO	0.02–0.98	2/3	56.5 ± 0.6	2.92×10^{24}	3.9
$NiC_2O_4 \cdot 2\ H_2O$	NiC_2O_4	0.06–0.95	2	60.4 ± 0.2	7.93×10^{24}	2.1
NiC_2O_4	Ni	0.01–0.97	1	183.0 ± 0.4	1.45×10^{65}	2.8
$CoC_2O_4 \cdot 2\ H_2O$	CoC_2O_4	0.04–0.94	1	37.7 ± 0.3	5.37×10^{15}	5.4
CoC_2O_4	Co	0.02–0.97	2	47.4 ± 0.7	1.11×10^{15}	7.2
CuC_2O_4	Cu	0.03–0.94	2	159.0 ± 1.1	1.39×10^{67}	7.3
PbC_2O_4	Pb	0.04–0.98	2	129.0 ± 0.9	2.88×10^{43}	6.9
$FeC_2O_4 \cdot 2\ H_2O$	FeC_2O_4	0.04–0.99	2/3	25.4 ± 0.4	3.33×10^{9}	6.2
FeC_2O_4	Fe	0.03–0.98	2	27.0 ± 0.3	2.50×10^{8}	4.6

$Ba(OH)_2 \cdot 6\,H_2O$	$Ba(OH)_2$	0.01–0.97	2/3	21.2 ± 0.5	2.35×10^{11}	5.5
$Ba(OH)_2$	BaO	0.03–0.96	2/3	53.7 ± 0.7	1.34×10^{30}	6.2
$Ca(OH)_2$	CaO	0.02–0.90	2/3	43.2 ± 0.3	1.94×10^{11}	4.7
$Mg(OH)_2$	MgO	0.06–0.92	2	88.8 ± 1.1	3.96×10^{28}	8.2
$Al(OH)_3$	Al_2O_3	0.10–0.78	2/3	77.7 ± 0.7	9.24×10^{29}	7.8
$Zn(OH)_2$	ZnO	0.06–0.99	2	90.4 ± 0.8	2.78×10^{32}	8.4
$Ca(CH_3COO)_2$	$CaCO_3$	0.02–0.37	2	34.0 ± 0.6	2.10×10^{7}	7.9
		0.37–0.98	2	47.3 ± 0.5	6.94×10^{11}	6.2
$Ba(CH_3COO)_2$	$BaCO_3$	0.04–0.10	1	114.0 ± 0.4	2.23×10^{31}	4.4
		0.10–0.98	1	316.0 ± 0.5	1.49×10^{92}	5.1
$Al(OH)(CH_3COO)_2 \cdot H_2O$	$Al(OH)(CH_3COO)_2$	0.03–0.97	2/3	20.9 ± 0.1	1.59×10^{11}	2.4
$Al(OH)(CH_3COO)_2$	Al_2O_3	0.03–0.64	2	28.0 ± 0.2	3.04×10^{8}	4.6
$Mg(CH$		0.64–0.92	2	14.5 ± 0.5	3.70×10^{2}	7.1
$Mg(CH_3COO)_2 \cdot 4\,H_2O$	$Mg(CH_3COO)_2$	0.02–0.95	2	36.4 ± 0.7	4.17×10^{20}	5.9
$Co(CH_3COO)_2 \cdot 2\,H_2O$	$Co(CH_3COO)_2$	0.01–0.97	2/3	27.6 ± 0.3	6.22×10^{13}	6.4
$Co(CH_3COO)_2$	$Co(CH_3CO)_2$	0.30–0.99	1	47.4 ± 0.2	2.01×10^{17}	3.1
$Co(CH_3CO)_2$	Co_3O_4	0.01–0.98	2/3	36.9 ± 0.7	5.57×10^{10}	6.2
$Cu(CH_3COO)_2 \cdot H_2O$	$Cu(CH_3COO)_2$	0.06–0.97	2/3	25.3 ± 0.2	1.99×10^{11}	4.7
$Cu(CH_3COO)_2$	$Cu_2O \cdot CuO$	0.01–0.97	2/3	33.7 ± 0.6	2.69×10^{12}	6.3
$Pb(CH_3COO)_2 \cdot 2\,H_2O$	$Pb(CH_3COO)_2$	0.04–0.98	1	19.0 ± 0.2	3.24×10^{10}	3.4
$Pb(CH_3COO)_2$	$PbCO_3$	0.05–0.99	2	32.0 ± 1.1	1.30×10^{11}	6.5
$PbCO_3$	PbO	0.05–0.16	2/3	56.1 ± 0.1	5.19×10^{17}	2.1
		0.16–0.95	2/3	64.0 ± 0.2	1.61×10^{20}	3.5
$Zn(COOH)_2 \cdot 2\,H_2O$	$Zn(COOH)_2$	0.03–0.97	1	38.3 ± 0.2	4.66×10^{19}	3.9
$Zn(COOH)_2$	ZnO	0.03–0.45	1	22.0 ± 0.2	2.96×10^{5}	4.2
		0.45–0.97	1	99.8 ± 0.1	1.95×10^{36}	2.5

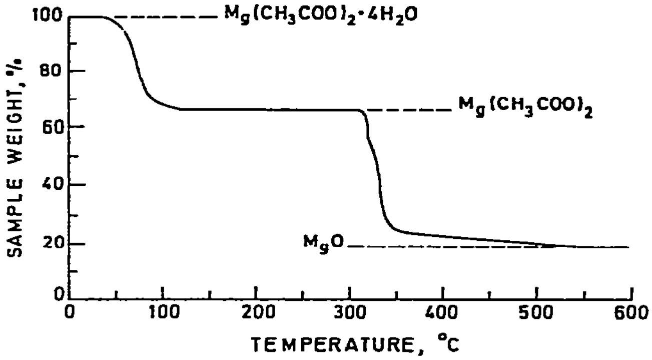

Fig. 3. Thermogravimetric results for magnesium acetate hydrate obtained at a heating rate of 1°C min^{-1} (20—600°C).

tion [10]. Further details on procedure may be found in Mu and Perlmutter [4]. A summary of the corresponding results for a variety of the salts studied is given in Table 3, but it should be emphasized that many of the decompositions examined followed rate patterns that were impossible to model by eqn. (1), possibly due to diffusional resistance in the solid reactant. In Figs. 2 and 3 for example, data are reproduced for $NiCO_3$ and $Mg(CH_3COO)_2 \cdot 4\ H_2O$, neither of which follows *n*-th order kinetics.

Effect of gas atmosphere

The oxylates studied were found to decompose differently in nitrogen or air atmospheres, not only with respect to kinetics, but also in terms of the

TABLE 4

Effect of oxidizing atmosphere on compounds formed in TG

Heating rate: 1°C min^{-1}; atmosphere: air.

Compound	Temp. (°C)	
	Initial reaction	Final reaction
$MnC_2O_4 \cdot 2\ H_2O$	115	150
MnC_2O_4	200	270
$3\ MnO_2 \cdot Mn_2O_3$	305	330
$Mn_3O_4 \cdot 2\ MnO_2$	>350	
$NiC_2O_4 \cdot 2\ H_2O$	135	260
NiC_2O_4	255	350
NiO	>360	
$CoC_2O_4 \cdot 2\ H_2O$	130	200
CoC_2O_4	225	275
Co_3O_4	>400	
CuC_2O_4	185	280
CuO	>300	
PbC_2O_4	270	345
PbO	>450	

TABLE 5

Kinetic parameters for reactions of oxalates in air

Compound		Conversion range for regression fit	Reaction order	Energy of activation (kcal gmole^{-1})	Pre-exponential parameter (sec^{-1})	Standard error (%)
Initial	Final					
MnC_2O_4	$3\ MnO_2 \cdot Mn_2O_3$	0.03–0.98	1	58.2 ± 0.6	1.47×10^{22}	4.4
NiC_2O_4	NiO	0.03–0.91	2	91.2 ± 0.3	6.42×10^{21}	2.5
CoC_2O_4	Co_3O_4	0.05–0.89	2	109.0 ± 0.6	6.95×10^{76}	4.1
CuC_2O_4	CuO	0.04–0.94	1	95.7 ± 1.3	2.05×10^{38}	7.6
PbC_2O_4	PbO	0.04–0.99	1	92.8 ± 0.7	6.05×10^{30}	5.2

specific intermediate and final products. Tables 4 and 5 report the compounds found and the decomposition kinetics, respectively, for the decompositions in air. These results should be compared with the same starting materials listed in Tables 2 and 3 to put in evidence the effects of inert or oxidizing surroundings. In other cases, the oxalates of calcium, magnesium, barium, and iron were evaluated in both atmospheres, but did not show any detectable difference in decomposition behavior. The results reported in Tables 2 and 3 cover the air studies as well as those under nitrogen.

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NOTATION

E	activation energy
k_0	frequency factor
n	order of reaction
R	gas constant
t	reaction time
T	reaction temperature
α	fractional conversion of the decomposing solid

REFERENCES

1 F.R. Campbell, A.W.D. Hills and A. Paulin, Chem. Eng. Sci., 25 (1970) 929.
2 R. Wagner, in G. Brauer (Ed.), Handbook of Preparative Inorganic Chemistry, Academic Press, New York, 1965.
3 K.E. Cox, Los Alamos Scientific Laboratory Report LA-6970-PR, 1977.
4 J. Mu and D.D. Perlmutter, Ind. Eng. Chem. Process Des. Dev., in press.
5 J. Palanisamy, Thermochim. Acta, 2 (1971) 265.
6 C. Duval, Inorganic Thermal Analysis, Elsevier, Amsterdam, 2nd edn., 1963.
7 D. Dollimore and D. Nicholson, J. Chem. Soc., (1963) 2617.
8 H.G. McAdie and J.M. Jervis, Thermochim. Acta, 1 (1970) 19.
9 D.A. Young, Decomposition of Solids, Pergamon Press, Oxford, 1966.
10 C.A. Bennett and N.L. Franklin, Statistical Analysis in Chemistry and the Chemical Industry, Wiley, New York, 1954.