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THERMAL DECOMPOSITION OF METAL NITRATES AND THEIR HYDRATES

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ABSTRACT

A study is reported of the controlled decompositions of various metal nitrates and their common hydrates, carried out in a thermogravimetric analyzer, a differential scanning calorimeter, and a differential thermal analyzer. Various sample sizes and heating rates 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.

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

INTRODUCTION

The thermal decomposition of common metal nitrates is an important class of reactions in the chemical industry with applications in the preparation of high surface area materials for catalysts, molecular sieves, and adsorbents [1], as well as of interest for ecological and environmental reasons [2].

In the study reported here, a series of ten metal nitrate hydrates were dehydrated and 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

TABLE 1

Sample compositions

Specifications in wt. %

Compound	Assay	Insoluble in HCl	Chloride	Sulfate	Fe	Pb	Cu	Others
$Ni(NO_3)_2 \cdot 6\,H_2O$	99.0	0.005	0.001	0.002	0 001	0.002	0.0005	Co=0.05 Zn=0.01
$Co(NO_3)_2 \cdot 6\,H_2O$	99.0	0.006	0 001	0.003	0 001	0.001	0.0001	Ni=0.008 Zn=0.001
$Al(NO_3)_3 \cdot 9\,H_2O$	98.0	0.005	0.001	0.005	0.005			Heavy metals=0.001
$Zn(NO_3)_2 \cdot 6\,H_2O$	99.0	0.005	0.002	0.005	0 0005	0.005	0.0005	
$Fe(NO_3)_3 \cdot 9\,H_2O$	99.0	0.005	0.000005	0 1				Mn=0.005
$Cr(NO_3)_3 \cdot 9\,H_2O$	98.0	0.01	0.002	0.008	0 005			Ammonium=0.002
$Cu(NO_3)_2 \cdot 2.5\,H_2O$	99.0 as $Cu(NO_3)_2 \cdot 3\,H_2O$	0.01	0.002	0 005	0.005	0.001		
$AgNO_3$	99.8	0.006	0.0002	0 0005	0.0001	0.0005	0.00003	
$Pb(NO_3)_2$	99.0	0.005	0.000005		0.001		0.002	
$Mg(NO_3)_2 \cdot 6\,H_2O$	99.0	0.001	0.0005	0.001	0 0001	0.0001		Phosphate=0.001 Ammonium=0.001 Ba=0.001 Na=0.001 Ca=0.002 Sr=0.001 Mn=0.0002 K=0.001

kinetics. Kinetic studies of such reactions are rarely truly isothermal, for it is very difficult to establish an isothermal condition before a substantial degree of reaction has occurred in the solid. When this is the case, dynamic techniques are preferable since they monitor the change of a selected parameter in a sufficiently large temperature interval continuously. Such rate studies are often run in thermogravimetric analyzers (TGA) at relatively high heating rates, (10°C min^{-1} or 20°C min^{-1}), but slower rates are needed to avoid endothermic temperature inhomogenieties and possible temperature gradients between a gas phase and a solid reactant. Furthermore, many salt hydrates have stable intermediate hydrates, some which are completely masked at high heating rates [3].

EXPERIMENTAL

The samples used in the decomposition studies reported here were all obtained as Baker Analyzed Reagent grade. 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 10°C min^{-1}. Sample weights were kept between 10 and 20 mg as suggested by previous workers, and a 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. After the preliminary tests were finished, TGA runs for the same materials were conducted at the slower heating rate of 1°C min^{-1} over the temperature ranges of interest, for more accurate determination of the various decomposition temperature 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 decompositions. A typical TGA thermogram is reproduced for reference as Fig. 1.

TABLE 2

Compositions identified by TG

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

Compound	Temperatures (°C)	
	Initial decomposition	Final decomposition
$Ni(NO_3)_2 \cdot 6\ H_2O$	30	60
$Ni(NO_3)_2 \cdot 4.5\ H_2O$	70	95
$Ni(NO_3)_2 \cdot 3\ H_2O$	105	167
$Ni(NO_3)_2 \cdot 1.5\ H_2O$	172	205
$Ni(NO_3)_2$	210	310
NiO	>350	
$Co(NO_3)_2 \cdot 6\ H_2O$	26	50
$Co(NO_3)_2 \cdot 4.5\ H_2O$	55	85
$Co(NO_3)_2 \cdot 2\ H_2O$	95	125
$Co(NO_3)_2 \cdot H_2O$	130	170
$Co(NO_3)_2$	185	310
Co_3O_4	>350	
$Mg(NO_3)_2 \cdot 6\ H_2O$	48	285
$Mg(NO_3)_2$	290	410
MgO	>450	
$Al(NO_3)_2 \cdot 9\ H_2O$	35	71
$Al(NO_3)_3 \cdot 6.5\ H_2O$	76	365
Al_2O_3	>450	
$Zn(NO_3)_2\ 6\ H_2O$	27	145
$Zn(NO_3)_2$	135	260
ZnO	>300	
$Fe(NO_3)_3 \cdot 9\ H_2O$	32	140
$Fe(NO_3)_3$	130	210
Fe_2O_3	>280	
$Cr(NO_3)_3 \cdot 9\ H_2O$	43	90
$Cr(NO_3)_3 \cdot 4.5\ H_2O$	102	260
CrO_3	>300	
$Cu(NO_3)_2 \cdot 2.5\ H_2O$	68	165
$Cu(NO_3)_2 \cdot 2\ Cu(OH)_2$	175	390
CuO	>450	
$AgNO_3$	285	415
Ag	>450 (melted)	
$Pb(NO_3)_2$	335	455
PbO	>500	

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

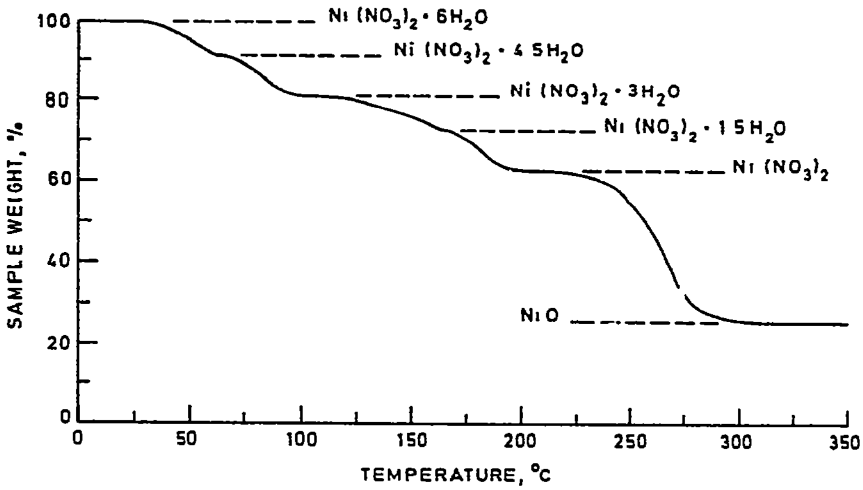

Fig. 1. Thermogravimetric results for nickel nitrate hydrate obtained at a heating rate of 1°C min^{-1} (20–350°C)

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 then 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 20–50°C higher than found at 1°C min^{-1}, and for some salts, e.g., $Co(NO_3)_2$, $Mg(NO_3)_2$, and $Zn(NO_3)_2$, the intermediate compounds could not be detected.

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

$$d\alpha/dt = k_0(1-\alpha)^n \exp(-E/RT) \quad (1)$$

is a convenient basis for comparison, since it subsumes most of the prior nucleation and diffusion models [5]. 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* distribution [6]. Further details on procedure may be found in ref. 4. A summary of the corresponding results for a variety of salts studied is given as 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

TABLE 3

Kinetic parameters for decompositions under nitrogen

Compound: Initial	Compound: Final	Conversion range for regression fit	Reaction order	Energy of activation (kcal $gmole^{-1}$)	Pre-exponential parameter (sec^{-1})	Standard error percentage
$Ni(NO_3)_2 \cdot 6\,H_2O$	$Ni(NO_3)_2 \cdot 4.5\,H_2O$	0.04–0 97	1	28.4 ±0.1	2.74×10^{16}	2.3
$Ni(NO_3)_2 \cdot 4.5\,H_2O$	$Ni(NO_3)_2 \cdot 3\,H_2O$	0.06–0.87	1	37.3 ±0.3	1.53×10^{20}	4.8
$Ni(NO_3)_2 \cdot 3\,H_2O$	$Ni(NO_3)_2 \cdot 1.5\,H_2O$	0.09–0.96	1	45.8 ±0 4	5.82×10^{20}	3.7
$Ni(NO_3)_2 \cdot 1.5\,H_2O$	$Ni(NO_3)_2$	0.03–0.79	2	29.5 ±0.3	5.87×10^{11}	3.2
$Ni(NO_3)_2$	NiO	0.02–0.96	1	48 6 ±0.2	5.76×19^{16}	3.1
$Co(NO_3)_2 \cdot 6\,H_2O$	$Cr(NO_3)_2 \cdot 4.5\,H_2O$	0.04–0.96	1/2	25.8 ±0.3	8.32×10^{21}	6.2
$Co(NO_3)_2 \cdot 4.5\,H_2O$	$Cr(NO_3)_2 \cdot 2\,H_2O$	0.08–0.94	2	43.9 ±0.4	$1\ 84 \times 10^{25}$	4.9
$Co(NO_3)_2 \cdot 2\,H_2O$	$Co(NO_3)_2 \cdot H_2O$	0.07–0.95	1	49.9 ±0.2	2.46×10^{25}	2.8
$Co(NO_3)_2 \cdot H_2O$	$Co(NO_3)_2$	0.04–0.93	1/2	19.9 ±0.3	7.57×10^{6}	3.2
$Co(NO_3)_2$	Co_3O_4	0.03–0.89	2	52.1± 0.8	1.64×10^{20}	4.4
$Mg(NO_3)_2$	MgO	0.04–0.24	2/3	28.2 ±0.5	3.64×10^{5}	4.6
		0 24–0.99	2/3	95.0± 0.9	8.16×10^{27}	7.8
$Al(NO_3)_3 \cdot 9\,H_2O$	$Al(NO_3)_3 \cdot 6.5\,H_2O$	0.02–0.94	1/2	9.36±0.4	1.17×10^{3}	3.6
$Zn(NO_3)_2 \cdot 6\,H_2O$	$Zn(NO_3)_2$	0.03–0.94	2	9 80±0.6	1.17×10^{3}	5.6
$Zn(NO_3)_2$	ZnO	0.02–0.99	2/3	14.2± 0.3	7.80×10^{2}	3.7
$Fe(NO_3)_3 \cdot 9\,H_2O$	$Fe(NO_3)_3$	0 04–0.53	2	15.6 ±0.6	8.47×10^{6}	6.2
		0.53–0.96	2	8.27±0.7	1.90×10^{2}	7.3
$FE(NO_3)_3$	Fe_2O_3	0.02–0.81	2/3	90.1 ±0.3	2.60×10^{44}	5.9
$Cr(NO_3)_3 \cdot 9\,H_2O$	$Cr(NO_3)_3 \cdot 4.5\,H_2O$	0.01–0.97	2	30.8 ±0.4	9.15×10^{16}	4.6
$Cu(NO_3)_2 \cdot 2.5\,H_2O$	$Cu(NO_3)_2 \cdot 2\,Cu(OH)_2$	0.03–0.65	2	20.6 ±0 5	1.38×10^{8}	5.2
		0 65–0.98	2	48.7 ±0.3	1.02×10^{24}	4.9
$Cu(NO_3)_2 \cdot 2\,Cu(OH)_2$	CuO	0.04–0.88	1	66.5 ±0.2	1.19×10^{27}	2.4
$AgNO_3$	Ag	0.03–0.26	2	48 9 ±0.2	1.43×10^{13}	3.2
		0.26–0.93	0	41.8 ±0.3	1.22×10^{10}	4.3

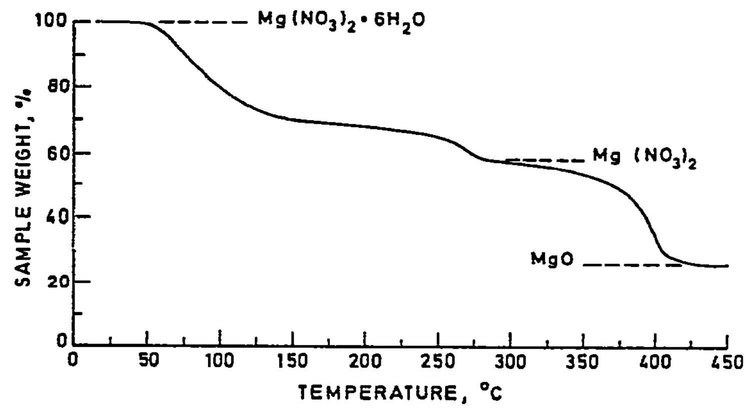

Fig. 2. Thermogravimetric results for magnesium nitrate hydrate obtained at a heating rate of 1°C min^{-1} (20–500°C).

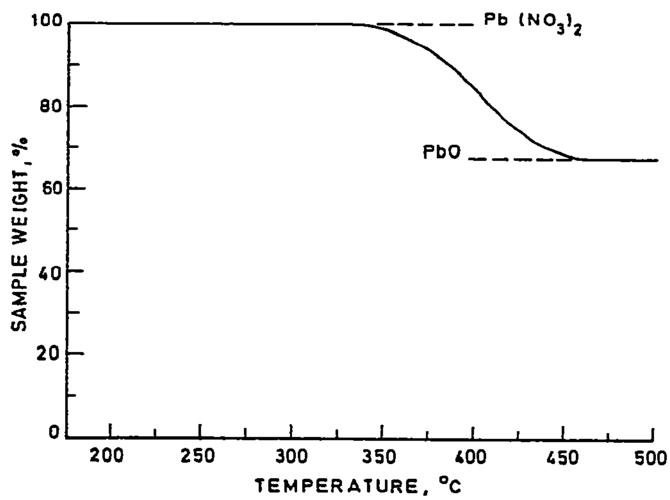

Fig. 3. Thermogravimetric results for lead nitrate obtained at a heating rate of 1°C min^{-1} (20–500°C).

are reproduced for $Mg(NO_3)_2 \cdot 6H_2O$ and $Pb(NO_3)_2$, neither of which follows *n*th order kinetics.

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