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Thermochimica Acta 261 (1995) 125–139

thermochimica
acta

Thermal analysis of anhydrous mixtures of calcium nitrate and selected metal oxides

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Received 18 October 1994; accepted 19 February 1995

Abstract

A thermoanalytical study has been made of the physical and chemical changes that occur on heating equimolar mixtures of $Ca(NO_3)_2$ and sixteen selected oxides that include those of the metals of the first transition period. The work was undertaken to characterize the factors that determine the rates of thermal anion breakdown in these mixtures of initially solid reactants. It was also of interest, for environmental reasons, to investigate the stability and chemistry of $Ca(NO_3)_2$. This compound is a possible intermediate or participant in those purification treatments of power station effluent gases that use $CaCO_3$ to remove the combustion products that lead to acid rain (SO_x and NO_x).

Decompositions of most metal-oxide-containing mixtures occurred close to the melting point of pure $Ca(NO_3)_2$, 563°C, and appreciably below its decomposition point, 675°C. We conclude that the promotional activity of each metal oxide results from reaction to form a metal nitrate in the melt which initially contains Ca^{2+}, M^{n+}, O^{2-} and NO_3^-. Mixtures containing oxides of metals of the first transition series commenced NO_3^- decomposition at relatively low temperatures; those with partially filled d-shells were most active, i.e. Mn^{2+}, Fe^{3+} followed by Cr^{3+} and Co^{2+}. Other oxides only promoted decomposition after $Ca(NO_3)_2$ fusion. We conclude that the dominant factor controlling the decomposition of calcium nitrate is melting. Oxides of metals of the first transition period significantly catalysed NO_3^- breakdown probably through nitrite formation and cation participation in electron transfer steps. Reaction mechanisms are discussed.

Keywords: Calcium nitrate; Metal oxides; TA

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SSDI 0040-6031(95)02314-3

1. Introduction

This paper reports an investigation into the chemical aspects of a possible use of $Ca(NO_3)_2$ for the denitrification of flue gases from coal combustion during electricity generation. The gaseous effluents from power station furnaces contain oxides of nitrogen and sulphur ($NO_x + SO_x$) that have been identified as major contributors to acid rain [1]. Considerable effort has been directed towards developing gas-cleaning processes whereby such pollution can be reduced. The present contribution represents part of an ongoing research programme undertaken to extend our understanding of the fundamental chemistry that may be applied to increase the efficiency and effectiveness of the removal of the precursors to acid rain.

We have investigated aspects of the reactions of NO_x and SO_x with $CaCO_3$ that may be used to remove these gases before discharge to the atmosphere. Insights into the factors controlling the rates and the mechanisms of the significant participating chemical steps can be expected to be employed in the design of gas effluent treatment methods. Any improvement will lead to a diminution of environmental stress.

The chemistry of the various reactions that yield $CaSO_4$ from the interaction of SO_2 with $CaCO_3(Ca(OH)_2$ or $CaO)$ under oxidizing conditions has been the subject of numerous studies, amongst which the following examples may be cited [2–6]. Very much less attention has, however, been given to denitrification, NO_2 removal, and the possible participation of NO_2 and/or $Ca(NO_3)_2$ in desulphurization reactions. It is known [7, 8] that NO_2 reacts with calcite or calcium hydroxide to form $Ca(NO_3)_2$ above 150°C so that transitory nitrate intervention may be involved at the lowest temperatures of flue gas treatment with calcium carbonate. The thermal decomposition of $Ca(NO_3)_2$ has been studied [9].

In the present paper, we have investigated the catalytic activities of a representative range of different and varied metal oxides for the promotion of anion breakdown on heating $Ca(NO_3)_2$. The decomposition products were also considered because the formation of non-polluting oxygen and nitrogen from calcium nitrate would offer a useful route for the denitrification of flue gases. The formation of these products requires a change of mechanism because NO_3^- breakdown in $Ca(NO_3)_2$ yields mainly oxides of nitrogen [9]. The influence of nitrate on desulphurization, referred to above, has been the subject of a different study that we intend to publish later.

Decompositions of the $Ca(NO_3)_2$ + oxide mixtures were studied by differential scanning calorimetry (DSC) and the observations were compared with the behaviour of the pure salt under identical conditions. When heated at constant rate (10°C min^{-1}), anhydrous $Ca(NO_3)_2$ melted at approx. 563°C and the endothermic anion breakdown was completed by approx. 675°C.

Another reason for undertaking the present work was to determine the chemical and physical factors controlling the steps participating in this group of related reactions. It was of interest to establish whether the promotional activities of a range of diverse added oxides on $Ca(NO_3)_2$ breakdown could be correlated with any chemical property of the cation present in the added oxide. Oxides selected for study included those of the first transition period metals, for which the catalytic reactivities were systematically compared. These observations were complemented with similar measurements for oxides expected to be less reactive (MgO, Al_2O_3 and TiO_2), together with others regarded as potentially reactive (PtO, PbO and PbO_2). Measurements also included consideration of whether reactions proceeded with the intervention of the metal nitrate of the cation present. If this occurred, catalytic activity could be ascribed to the formation of an intermediate metal nitrate, relatively less stable than $Ca(NO_3)_2$. Aspects of the stoichiometry of anion breakdown were determined from the measured enthalpies of melting and (usually) the subsequent endothermic decomposition, and weight loss measurements. Attention was also directed towards establishing the role of melting in these reactions and whether the oxides studied were capable of promoting anion breakdown in the solid state. It is sometimes difficult to establish whether decompositions of solid reactants involve partial or local melting [10, 11] or proceed with the participation of a liquid intermediate [12] or product [13]. The kinetic characteristics of reactions proceeding in a homogeneous phase, but in the absence of added solvent, through partial or complete melting, have not been extensively investigated [14]. Aspects of the properties of such rate processes, in a melt or in a solid + melt mixture, were of interest in considering the mechanisms and rate-controlling parameters in the present sequence of reactions.

Because nitrate anion breakdown is endothermic, it was expected that the catalytic promotion by metal oxides would be relatively small. This was confirmed and most results give strong evidence that decomposition proceeded in a salt melt.

2. Experimental

2.1. *Reactant mixtures*

All reactants studied contained (weighed) equimolar proportions of the selected oxide and anhydrous calcium nitrate that had previously been dried for 30 min at 190°C. The components of each reactant were thoroughly mixed by grinding together in a pestle and mortar. Present interest was centred almost exclusively upon processes occurring above 500°C. In a limited number of experiments, some very small endothermic responses between about 370 and 400°C were detected which may have resulted from incompletely dehydrated salt or its partial rehydration during brief exposure to the atmosphere. The oxides used were laboratory or reagent grade and supplied by a variety of manufacturers.

2.2. *Apparatus*

Thermal analysis measurements were performed in a Perkin-Elmer differential scanning calorimeter, DSC 7, using the standard PC DSC 7 computer program supplied by the manufacturer. Weighed samples of each reactant mixture, usually between 10 and 20 mg, were contained in gold pans and heated at $10°C\ min^{-1}$ in a constant flow of $30\ cm^3 N_2\ min^{-1}$. An empty gold pan was used as reference. The mass of each residual product was determined after cooling. All experiments were carried out in duplicate and response temperatures were mean values obtained only from experiments that showed acceptable reproducibility.

3. Results and discussion

3.1. Pure anhydrous calcium nitrate

A typical DSC reponse trace across the temperature interval that includes both melting and decomposition of anhydrous calcium nitrate (without additives) is shown in Fig. 1. Some features of this reaction showed significant irreproducibility and, to characterize behaviour reliably, some 50 individual experiments were completed for heating rates of 10°C min^{-1}. This detailed comparison was regarded as essential to establish, with confidence, the behaviour pattern for the pure salt before measuring the influences of additives. (All oxide-containing mixtures showed much less variation between duplicate identical experiments.)

The lowest temperature sharp response was identified as $Ca(NO_3)_2$ melting for which the mean temperature was 563.2 ± 2.5°C and the mean enthalpy was 38.3 ± 1.2 kJ mol^{-1}. This always preceded the endotherms identified with the anion decomposition reactions, confirming that nitrate breakdown occurred in a melt.

The maximum temperature mean for the large endotherm associated with the main decomposition reaction was 675 ± 4°C and reaction was completed by 683 ± 6°C. This peak overlapped with, and sometimes largely obscured, an earlier smaller maximum with a mean peak temperature estimated to be 660 ± 8°C. The enthalpy of

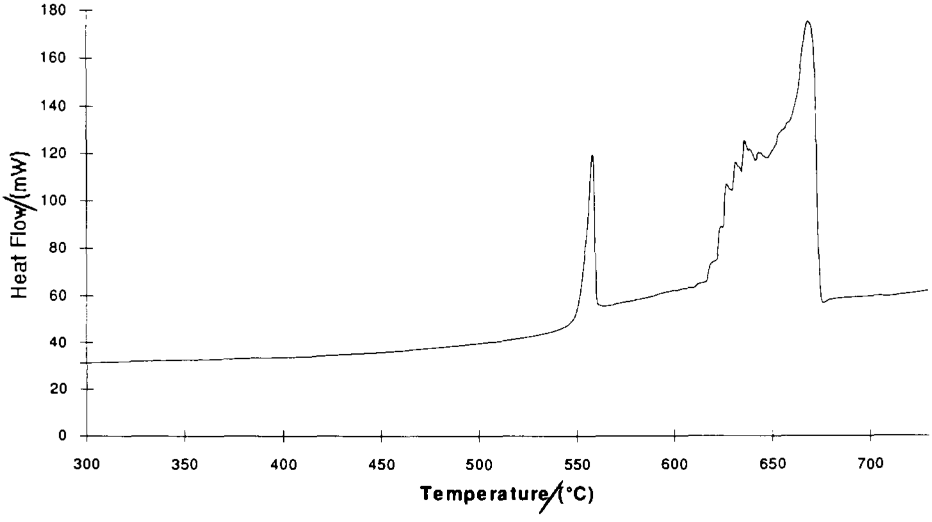

Fig. 1. Representative DSC traces for melting and decomposition on heating anhydrous $Ca(NO_3)_2$ at 10°C min^{-1} in a flow of nitrogen (30 cm^3 min^{-1}).

decomposition of $Ca(NO_3)_2$ was 451 ± 9 kJ mol^{-1}, mean overall estimated values extended to include both melting and decomposition were 558 ± 40 kJ mol^{-1}.

Irreproducibility, evident in the detailed pattern of decomposition response peaks after melting, was associated with the retention of water by the reactant. Samples for which small low-temperature (155–180°C) responses (identified as water evolution) were detected tended to complete decomposition at temperatures lower than average. On heating samples of hydrated $Ca(NO_3)_2$, decomposition was sometimes completed at as low as 640°C, following a main endotherm maximum between 610 and 630°C. The highest decomposition temperatures were found using small masses of anhydrous salt, conditions expected to minimize water retention.

In systematic comparative studies it was shown that the DSC response pattern for anhydrous $Ca(NO_3)_2$ decomposition was independent of reactant mass (2–16 mg), of salt dispersal within the pan, and of crystal pre-crushing. All these features are consistent with the completion of melting before reaction whereby textural dissimilarities of the reactant particles are lost.

3.2. Equimolar crushed mixtures of anhydrous calcium nitrate and oxides of metals of the first transition period

Equimolar crushed mixtures of anhydrous $Ca(NO_3)_2$ and an oxide of a metal of the first transition period, contained in a gold pan, were heated in the DSC 7 apparatus at 10°C min^{-1} in a nitrogen flow. All response peaks, invariably endothermic, detected above 200°C are recorded in Table 1. Representative DSC traces are shown in Fig. 2. The first peak (Table 1), $T_1 \pm 3$°C, is identified as melting, though this response could not always be resolved because of overlap with the larger subsequent endotherm. This

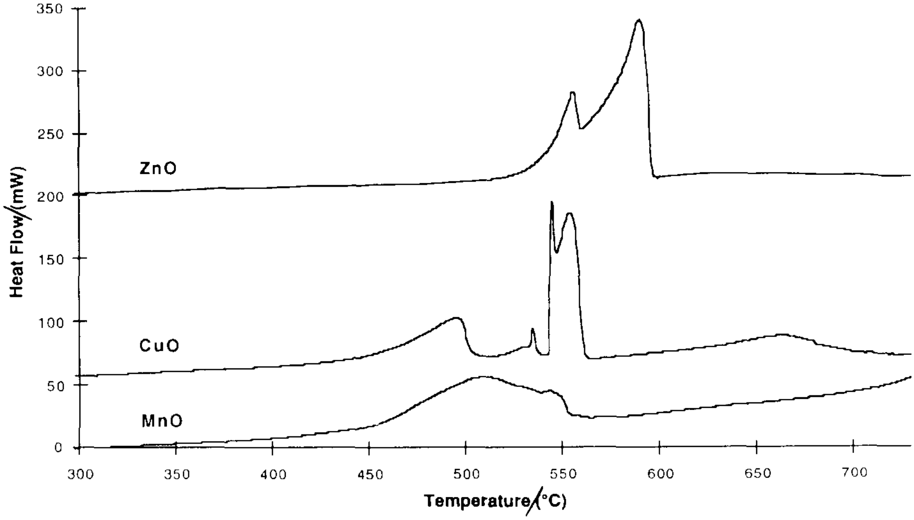

Fig. 2. Representative DSC traces on heating equimolar mixtures of anhydrous $Ca(NO_3)_2$ with CuO, ZnO or MnO at 10°C min^{-1} in a flow of nitrogen (30 cm^3 min^{-1}).

Table 1
Thermal reactions of equimolar mixtures of calcium nitrate and oxides of transition metals from the first transition period. Data from DSC response traces on heating at 10°C min^{-1} in nitrogen

Metal oxide	Melting point T_1 °C	Decomposition endotherm		Small peak T_4 °C	Weight loss % $Ca(NO_3)_2$ present	Decomposition and melting enthalpy kJ $(mol Ca(NO_3)_2)^{-1}$
		Maximum T_2 °C	Completed T_3 °C			
None	563.2	675	683	–	66.5	558
V_2O_5	562	587	604	445	69.3	231
Cr_2O_3	–	554	563	443	53.7	278
MnO	–	500–530	555	–	72.6	333
MnO_2	555(?)	567	575	–	66.0	456
Fe_2O_3	–	502, 570	582	320	89.5	632
CoO	–	530, 557	572	460	73.2	427
NiO	558	572	582	490	66.0	504
Cu_2O	495–500(?)	550	562	–	63.1	422
CuO	544	554	564	494	72.3	430
ZnO	557	595	602	–	69.4	495

dominant response, for anion decomposition, gave the maximum at $T_2 \pm 5°C$ and was completed at $T_3 \pm 5°C$. Where another small peak was detected, it was recorded as $T_4 \pm 5°C$. Table 1 also lists the weight loss on completion of reaction expressed as % of the $Ca(NO_3)_2$ originally present in the mixture: 66.5% corresponds to decomposition to CaO. Measured decomposition enthalpies, (mol $Ca(NO_3)_2)^{-1}$, are also included in Table 1. Comments for the individual oxide mixtures studied are given below. It was confirmed from literature sources and examinations of DSC traces that all oxides studied were stable below the temperatures of onset of interactions with the calcium nitrate in the mixtures studied.

V_2O_5

The large decomposition endotherm, maximum 562°C, is identified as melting and commenced just below the mean melting point for pure $Ca(NO_3)_2$. Anion breakdown is, therefore, promoted by the added oxide at the onset of salt melting. The reason for the second peak, 587°C, was not established but it could result from incomplete decomposition in the first stage or be due to reaction between the residual oxides (perhaps to give calcium vanadate).

Cr_2O_3

The large reaction endotherm at 554°C included no sharp response attributable to melting and indeed decomposition was completed at the melting point of the pure salt. Decomposition is strongly promoted and reaction may involve progressive melting in this oxidizing material [10]. Oxidation of Cr^{3+} accounts for the relatively small weight loss during this reaction that may yield calcium chromate, which is believed to be stable above 600°C: this explains the absence of any further response peak (compare magnesium chromate [15] and the melting points of Na_2CrO_4 (792°C) and K_2CrO_4 (975°C)).

MnO and MnO$_2$

Salt breakdown in the presence of either of these oxides gave two overlapping maxima that were not resolved. Decomposition of the mixture containing MnO commenced at 450°C, the lowest temperature recorded for any of the oxides investigated here, and reaction was complete at 555°C. This reactivity may arise through the intervention of $Mn(NO_3)_2$ known [16] to decompose between 140 and 200°C. The activity of MnO_2 was appreciably less and here the ill-resolved sharp maxima at 550°C suggest the overlapping of melting with rapid onset of decomposition and completion of reaction by 575°C.

The reactivity of MnO is ascribed to a facile reaction involving cation oxidation together with rapid decomposition of any manganese nitrate formed. Decomposition close to the salt melting point in both mixtures, however, is evidence that fusion enhances anion breakdown.

Fe$_2$O$_3$

The main decomposition occurred with an endothermic maximum at 502°C and a second, much smaller, response at 570°C (an unresolved doublet) followed by rapid completion of reaction by 582°C. Fe_2O_3 strongly promoted anion breakdown and, as with the manganese oxides, this close association of reaction with the salt melting point suggests the participation of fusion. This could be a reason for the subsidiary maximum at 570°C if decomposition follows fusion of a small proportion of salt ($\approx$ 10%) initially without contact with the oxide.

CoO

The first endotherm at about 530°C overlapped with the main response at 557°C which again suggests a significant role for fusion with completion of anion breakdown by 572°C, just above the melting point of the salt.

NiO

Decomposition proceeded to completion in two rate processes: the larger endotherm at 558°C was followed by the smaller at 572°C, before rapid completion of reaction by 582°C.

Similar measurements using an equimolar mixture of $Ca(NO_3)_2 + Ni(NO_3)_2$ gave two sharp endotherms with maxima at 546 and 551°C and completion of reaction by 557°C. This is very similar to the NiO-containing mixture which gave broader peaks at greater temperatures: +12°C for the first reaction and +21°C for the second. Allowing for the compositional differences between the two mixtures and the time required for $Ca(NO_3)_2$ to interact with NiO and form a mixture of molten nitrate containing both cations, these two patterns of behaviour can be regarded as closely similar. We conclude, therefore, that decomposition in the $Ca(NO_3)_2$ + NiO mixture probably proceeds with the intermediate formation of nickel nitrate.

Cu_2O and CuO

The largest endotherm maximum detected in each of the reaction mixtures of $Ca(NO_3)_2$ with Cu_2O (550°C), with CuO (554°C) or with copper nitrate (two peaks at 555 and 560°C) was sufficiently close for us to conclude that the same reaction steps controlled the decompositions of all three mixtures. The CuO- and $Cu(NO_3)_2$-containing mixtures commenced with sharp endotherms at 554°C that can be identified as fusion occurring slightly below the melting point for the pure salt. The low temperature onset of reaction of the Cu_2O-containing mixture (an unresolved endotherm at 500°C) can be ascribed to an initial copper oxidation step (reaction temperatures were similar to those for MnO where there is also the possibility of cation oxidation). The weight loss measurements suggest that residues from reactions of both oxides contain both Cu_2O and CuO. We conclude from the similarities in behaviour that reactions proceed in a melt with the intervention of copper(II) nitrate.

ZnO

The initial sharp endotherm (557°C) is identified as melting, followed by a decomposition endotherm (595°C) with rapid completion of reaction (602°C) well below the temperature for anion breakdown in the pure salt.

3.3. *Equimolar crushed mixtures of anhydrous calcium nitrate and selected oxides*

Identical DSC studies were made for equimolar crushed mixtures of $Ca(NO_3)_2$ with other oxides, selected for the following reasons. MgO, Al_2O_3 and TiO_2 contained cations that were expected not to undergo valence changes during nitrate breakdown. PtO was included because platinum metal is active in nitrogen oxidation reactions (as in nitric acid manufacture). It was also demonstrated separately that Pt metal did not detectably promote $Ca(NO_3)_2$ decomposition. PbO and PbO_2 compared the behaviour of this cation in two valence states.

Mean values of all the endothermic peaks detected throughout these studies are recorded in Table 2. Temperature values recorded and estimated accuracies are as specified for Table 1. The PbO_2 response at 530°C is less reliable because it overlapped with the larger peak following. The $Ca(NO_3)_2 + MgO$ mixture showed two additional small endotherms at 385 and 617°C.

MgO, Al_2O_3 and TiO_2

The endothermic responses for these three mixtures were similar and results are conveniently considered together. Mixtures containing each of these oxides gave endothermic responses close to the melting point of pure $Ca(NO_3)_2$. These peaks were, however, broadened compared with the pure salt and those of MgO and Al_2O_3 occurred at slightly reduced temperatures. This behaviour is believed to result from the incorporation of some cation from the oxide into the melt (nitrate formation).

The presence of Al_2O_3 (and Al^{3+}) or TiO_2 (and Ti^{4+}) in the melt reduced the decomposition temperature. Neither of these cations forms a stable nitrate but both, on the surfaces of the oxides added, appear to be capable of promoting anion breakdown.

Table 2
Thermal reactions of equimolar mixtures of calcium nitrate and selected metal oxides (oxide cations not from first transition period). Data from DSC response traces on heating at 10°C min^{-1} in nitrogen

Metal oxide	Melting point T_1°C	Decomposition endotherm		Weight loss % $Ca(NO_3)_2$ present	Decomposition and melting enthalpy kJ $(mol Ca(NO_3)_2)^{-1}$
		Maximum T_2°C	Completed T_3°C		
None	563.2	675	683	66.5	558
MgO	555	679	690	79.8	450
Al_2O_3	549	607	622	71.7	488
TiO_2	565	592	603	66.4	453
PtO	551	600	606	65.8	534
PbO	546	565	580	66.7	489
PbO_2	530(?)	556	570	77.2	494

It is alternatively possible that water, introduced as metal hydroxide, accelerated the reactions; this is supported by the relatively large weight losses measured for these reactions. The formation of volatile $Ti(NO_3)_4$ [17] can be excluded because no excess weight loss was found (Table 2).

The $Ca(NO_3)_2$ + MgO mixture gave additional endotherms at 385 and 617°C which were also detected in similar DSC studies for $Mg(NO_3)_2$. Values of T_2 and T_3 (Table 2) were in accordance with expectation for $Ca(NO_3)_2$. These results are ascribed to some $Mg(NO_3)_2$ formation early in the heating process and subsequent independent decompositions of the $Mg(NO_3)_2$ and the $Ca(NO_3)_2$ in the mixture.

PtO

Melting of this mixture was detected at a temperature below that of the pure salt. Subsequent decomposition was also promoted and Pt^{2+} (or PtO) is identified as a catalyst for nitrate anion breakdown.

PbO and PbO_2

The DSC curves for reactions of mixtures containing these oxides were similar (Fig. 3). The low temperature of melting, together with broadening of these endotherms to overlap with the subsequent decomposition response, is evidence that fusion, with possible formation of lead nitrate, is rapidly followed by anion breakdown. The relatively large weight loss from the PbO_2-containing mixture suggests the reactions include some cation reduction to PbO.

3.4. Comment

All these additives promoted $Ca(NO_3)_2$ decomposition; lead (PbO and PbO_2) was the most active but Al_2O_3 and TiO_2 may introduce water (hydroxide) into the melt. The reduction in temperature of the melting point endotherm, together with peak broadening, suggests that fusion is promoted by incorporation of cations from the

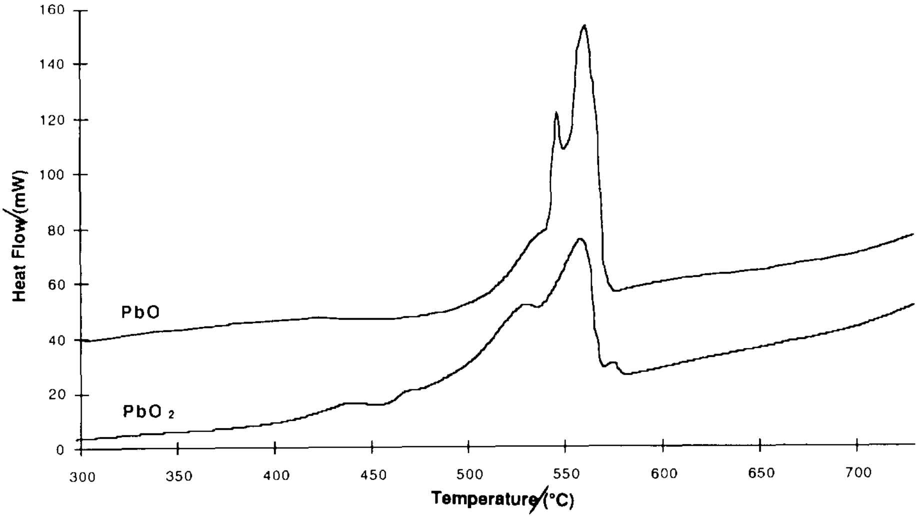

Fig. 3. Representative DSC traces on heating equimolar mixtures of anhydrous $Ca(NO_3)_2$ with PbO or PbO_2 at 10°C min^{-1} in a flow of nitrogen (30 cm^3 min^{-1}).

oxide with metal nitrate formation. All decompositions, except for the MgO-containing mixture, were completed at a temperature less than that of the pure salt.

3.5. *Mass losses*

The expected mass loss for the decomposition of $Ca(NO_3)_2$ to CaO was 66.5%. This was observed (Tables 1 and 2), within experimental error, for the mixtures containing V_2O_5, MnO_2, Fe_2O_3, NiO, ZnO, TiO_2, PtO and PbO. These reactions yield, therefore, CaO + unchanged oxide (or possibly a double oxide).

The relatively smaller mass losses from the mixtures containing Cr_2O_3 and Cu_2O may be identified as cation oxidation to chromate or to some CuO, respectively. The relatively larger mass losses from CuO and PbO_2 mixtures similarly may be due to cation reduction to Cu_2O and PbO. Residues from the two copper oxide mixtures are thus believed to contain both Cu_2O and CuO. The relatively large weight losses from the MnO and CoO mixtures are unexplained because reduction of these cations is not expected. This may result from strongly retained water or hydroxide in the mixture as with MgO and Al_2O_3, mentioned above.

3.6. *Reaction enthalpies*

Calculated enthalpies for the decomposition of $Ca(NO_3)_2$ at 560°C were as follows

$$Ca(NO_3)_2 \longrightarrow CaO + N_2 + 2.5O_2 \qquad \Delta H = +370\ \text{kJ mol}^{-1} \tag{1}$$

$$Ca(NO_3)_2 \longrightarrow CaO + 2NO + 1.5O_2 \qquad \Delta H = +456\ \text{kJ mol}^{-1} \tag{2}$$

$$Ca(NO_3)_2 \longrightarrow CaO + 2NO_2 + 0.5O_2 \qquad \Delta H = +430\ \text{kJ mol}^{-1} \tag{3}$$

The mean measured value reported above for the pure salt (451 ± 9 kJ $\mathrm{mol^{-1}}$) agrees well with expectation for a reaction that yields NO and some NO_2, and the contribution from reaction (1) is expected to be small.

Mixtures containing MnO_2, CoO, Cu_2O, CuO, MgO and TiO_2 gave (Tables 1 and 2) reaction enthalpies that are close to expectation for reactions (2) and (3); the differences may result from variations in product compositions. The low values for mixtures containing V_2O_5 and Cr_2O_3 may be due to the formation of calcium vanadate and calcium chromate. Other additives may similarly yield a double oxide or solid solution residual product.

It is interesting to note that (excluding the V_2O_5 and Cr_2O_3 mixtures which may react with CaO) the lowest reaction enthalpies (values below that for $Ca(NO_3)_2$) were found for the oxides that were identified as the most active catalysts for nitrate breakdown: MnO, Fe_2O_3, CoO, Cu_2O and CuO. This may indicate a relative increase of the contribution of reaction (1) in the catalysed process, a result that could be of value in denitrification of flue gases.

3.7. Decomposition of calcium nitrate

Pure $Ca(NO_3)_2$ decomposes at a temperature (675°C) appreciably above its melting point (563.2°C). The reaction is completed (683°C) in two distinct and consecutive rate processes that overlap (Fig. 1). This may be ascribed to stepwise anion breakdown, expressed by

$$Ca(NO_3)_2 \longrightarrow Ca(NO_2)_2 + O_2$$

$$Ca(NO_2)_2 \longrightarrow CaO + NO_2 + NO$$

The primary gaseous products may undergo further reactions at the decomposition temperature [18], e.g. [19]

$$Ca(NO_2)_2 + 2NO_2 \leftrightarrow Ca(NO_3)_2 + 2NO$$

$$Ca(NO_2)_2 + 2NO \rightarrow Ca(NO_3)_2 + N_2$$

The separation of the two decomposition rate processes (Fig. 1) may be regarded as evidence that nitrate breakdown does not promote nitrite breakdown. Reactions commence at temperatures of onset of N–O bond rupture in the anion, and may be represented by the following steps

$$2NO_3^- \longrightarrow O_2^-N\cdots\cdots O\cdots\cdots O\cdots\cdots NO_2^- \longrightarrow 2NO_2^- + O_2 \qquad (4)$$

$$2NO_2^- \longrightarrow O\text{–}N\text{–}O^- \; {}^-O\text{–}N\text{–}O \longrightarrow ON\cdots O^{2-}\cdots ONO \longrightarrow NO + NO_2 + O^{2-} \qquad (5)$$

3.8. Role of metal nitrate formation during decompositions of oxide + $Ca(NO_3)_2$ mixtures

Reaction of $Ca(NO_3)_2$ with added oxide at, or near, the salt melting point will yield a reactant fluid that initially contains Ca^{2+}, M^{n+}, O^{2-} and NO_3^-. Only the nitrate will decompose. The present observations cannot, however, be usefully compared with results for the decompositions of appropriate anhydrous nitrates because the necessary information is not available. Transition metal nitrates are frequently hydrated and temperatures of pyrolyses of the water-free salts are not reliably known. The evidence elicited, however, suggests that calcium nitrate is relatively stable and other nitrates decompose at lower temperatures: $Pb(NO_3)_2$ at approx. 300°C [18], $AgNO_3$ in a melt at approx. 450°C, and both $NaNO_3$ and KNO_3 below 400°C.

The close similarities between the DSC response peaks observed for the mixtures $Ca(NO_3)_2 + M(NO_3)_2$ where M is Ni, Cu or Mg, and the respective oxide-containing mixture, $MO + Ca(NO_3)_2$, suggests the probability of nitrate intervention in the latter. It has also been shown [8] that several (but not all) oxides studied here, Cu_2O, ZnO, PbO and ZnO, react with $NO_2 + O_2$ below 525°C to form metal nitrate. It may be concluded, therefore, that reactions resulting in intermediate nitrate production are very probable under conditions prevailing during the decompositions of $MO + Ca(NO_3)_2$ mixtures.

3.9. *Decompositions of $Ca(NO_3)_2$ + metal oxide mixtures*

Oxides significantly promoting $Ca(NO_3)_2$ breakdown (transition metal cations, platinum and lead) are listed in a sequence of diminishing activity in Table 3. While different criteria are used for the different classifications in the table, and the sequences in these change slightly, the same general trends in promotional activity are found for this group of oxides under all the headings shown.

Table 3
Oxides most active in promoting $Ca(NO_3)_2$ decomposition

Oxide	Melting point endotherm maximum °C	Endotherm maximum, reduction in temperature compared with pure salt		Reduction in temperature of completion of reaction compared to pure salt °C	Enthalpy of decomposition and melting kJ (mol $Ca(NO_3)_2)^{-1}$
		Larger peak °C	Smaller peak °C		
MnO	x	−175	−145	−128	333
Fe_2O_3	x	−173	−105	−101	632
Cr_2O_3	x	−121	–	−120	278
CoO	x	−118	−145	−111	427
Cu_2O, CuO	≈500	−125	–	−120	426
PbO, PbO_2	≈538	−115	–	−108	492
MnO_2	≈555	−108	–	−108	456
NiO	558	−103	–	−101	504
V_2O_5	562	−88	–	−79	231
TiO_2	565	−83	–	−80	453
ZnO	557	−80	–	−81	495
PtO	551	−75	–	−77	534

x, obscured by following large endotherm.

Correlations of these trends were sought, but none were found, with properties of the oxide cation, including ionic radius, ionization potential and oxidation e.m.f. A problem in this approach is the uncertainty in the oxidation state of the cation that is active for nitrate breakdown in the highly oxidizing reaction medium. A number of possibilities were considered but no acceptable explanation of the trend in Table 3 could be discerned. Also unsuccessful was a search for a comparable behaviour pattern to that in Table 3 in the papers by Winter concerned with reactions on oxide surfaces: O^{18} exchange [20] and decompositions of N_2O [21] and of NO [22]. These include several of the oxides studied here but surface areas may be different.

Most nitrate ion decompositions in the oxide-containing mixtures occur at temperatures close to the melting point of $Ca(NO_3)_2$ (563.2°C). All the oxides of metals from the first transition period (Table 1) significantly promoted NO_3^- decomposition while the activities of the other oxides were, with the exception of lead, somewhat less (Table 2). We also note that two pairs of oxides containing the same cations (Cu_2O, CuO; PbO, PbO_2) were closely similar, suggesting that these reacted to give the same participating active cation (or mixture of cations). We note, however, that the highly oxidizing form of manganese (MnO_2) was less active in this respect than MnO.

There is direct evidence from Tables 1 and 2 that most of the present reaction mixtures melt before or during reaction. Those mixtures that showed no such initial endotherm (MnO, Fe_2O_3, Cr_2O_3, CoO) included no distortion of the decomposition endotherm at about 563°C. From this we conclude that progressive melting occurs during these reactions through formation of a nitrate-containing melt (Ca^{2+}, M^{n+}, NO_3^- and O^{2-}). The evidence supporting the participation of metal nitrates has been discussed above. Reaction initiated at salt/oxide contacts can be expected to form mixed nitrate (or eutectic) melting below 563°C. For other oxides (Table 2), salt melting precedes decomposition.

The overall differences in the promotional activities for the cations studied are unexpectedly small. One possible explanation is that the reactivity is determined mainly by the stability of the nitrate ion and by the energy required for its endothermic decomposition. An alternative, and preferred, explanation is that NO_3^- breakdown is relatively rapid only following salt fusion and this is, therefore, an important reactivity control. This explains the occurrence of most endotherms relatively close to the $Ca(NO_3)_2$ fusion temperature.

On melting there is a loss of crystal stabilizing forces together with enhanced stereochemical freedom that enables reactant species to adopt the configuration most favourable to chemical change. Reaction in a liquid also avoids the deposition of product as a barrier layer that effectively separates reactant species [18]. Many solid reactants decompose with the participation of a liquid [10–14]. Apparent activation energy values calculated for the present decomposition endotherms were much larger than expected for chemical reactions; most were 400–700 kJ mol^{-1}. This is ascribed to concurrent processes, decomposition during progressive melting of the mix and/or nitrate formation. (The (notional) activation energy for melting is very large, perhaps infinite, because the melting rate proceeds from zero to a finite value in the fraction of a degree required to traverse the melting point.) Oxides of the first transition period metals promoted melting and nitrate formation below the melting point of the solid.

The oxides less active in catalysing decomposition gave no evidence of reaction until after salt melting. In both systems, NO_3^- breakdown occurs in a melt in which added active metal concentration is rising, thus accounting for the unusually large temperature coefficients of reaction rates.

3.10. *Reaction mechanisms*

The transitional metal cations with half-filled d-shells (Mn^{2+}, Fe^{3+}) showed greatest activity for NO_3^- ion breakdown, followed by the neighbouring elements in the periodic table (Cr^{3+}, Co^{2+}); the others were less active, see Table 3. The identification of activity with vacancies in the d-orbitals suggests that electron transfer steps explain the observed behaviour; compare with reactions (4) and (5) above

$$M^{n+} + {}^{-}O\text{–}NO_2 \longrightarrow M^{(n+1)+} + O^{2-} + NO_2$$

$$M^{(n+1)+} + {}^{-}O\text{–}NO_2 \longrightarrow M^{n+} + NO_3 \longrightarrow M^{n+} + 1/2O_2 + NO_2$$

The activities for the other oxides (Al_2O_3 and TiO_2) were not so readily explained but could be due to stereochemical advantages by reactions of anions co-ordinated with Al^{3+} or Ti^{4+} in the melt. There are also the possibilities that these oxides retain some water (hydroxide) that is thereby introduced into the melt or that the oxide surface promotes reaction [20–22].

4. Conclusions

The most significant conclusion from these observations for this group of related reactions is that a physical process, melting, is identified as the dominant control of reactivity. This possibility is not always considered in the interpretation of the thermal behaviour of initially solid reactants. Preferred reactions by a mechanism involving a liquid phase have been demonstrated for a number of processes for crystalline materials [10–14] and this model accounts satisfactorily for the present pattern of behaviour. In addition, we report evidence that several oxides catalyse NO_3^- breakdown, also promoting fusion and reaction in the mixed nitrate melt. Reaction temperatures are appreciably reduced by the cations present in the oxide, those undergoing the most facile valence changes being the most active. The magnitudes of the enthalpies of catalysed reactions provide little evidence that decompositions of these mixtures exclusively yield the more environmentally friendly products $N_2 + O_2$. These kinetic data are being used in further work intended to characterize more completely the gaseous decomposition products.

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