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# Infrared Spectra and Thermal Decomposition of Metal Nitrites and Nitrates[a]

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*The thermal decomposition of several metal nitrates and nitrites, particularly those of rare earths, have been investigated employing infrared spectroscopy to study the nature of the intermediates in these decompositions. The stoichiometry, kinetics, energetics and mechanism of the decompositions have beene discussed. Infrared spectra of metal nitrites have been studied in some detail and the normal vibration analysis of $AgNO_2$ is reported.*

## Introduction

The infrared spectra[1,2] and the thermal decomposition[3-5] of metal nitrates have received considerable attention in recent years. In metal nitrates where the covalency of the metal-oxygen bond is appreciable, metal-oxygen stretching bands have been observed in the far infrared region.[2] Since the nature of the thermal decomposition of nitrates should also depend on the strength of the metal-oxgen bond, it was considered interesting to examine the thermal decompositions of a variety of metal nitrates where the symmetry of the nitrate ion varies from $D_{3h}$ to $C_{2v}$. For this purpose, the thermal decompositions of silver and lead nitrates and several rare earth metal nitrates have been investigated employing thermogravimetric analysis as well as infrared and electronic spectroscopy. The decompositions of rare earth metal nitrates are of special interest since they are supposed to yield oxynitrates[3] or bridged nitrites[4-6] as intermediates. Since nitrites have been proposed as intermediates in the decomposition of metal nitrates[5,6] on the basis of the infrared spectra of partially decomposed nitrates, it was important to have information on the infrared spectra and thermal behaviour of metal nitrites.

The infrared spectra of metal nitrites have not been systematically examined in the literature;[7] the spectra of several metal nitrites, particularly those of rare earths, have been presently examined. Normal coordinate analysis of the in-plane vibrations of silver nitrite (which is known to have some covalency) has been carried out. The thermal decompositions of silver, lead and barium nitrites as well as several rare earth metal nitrites have been studied in fair detail.

## Results and Discussion

1. *Rare Earth Nitrites.* It has been stated in the literature that transition metals may not form nitrites and nitrites, if formed, readily transform to oxynitrates.[8] Elemental analyses, spectral evidence and thermal behaviour (see section 3) clearly show that rare earths do indeed form stable nitrites. The ultraviolet spectra of the rare earth nitrites in solution clearly show the band around 350 mμ with vibrational structure characteristic of nitrites. The infrared spectra of rare earth nitrites have been discussed at some length in the following section.

2. *Infrared Spectra of Metal Nitrites.* Ionic nitrites like sodium and potassium nitrites show bands due to $\nu_a$ and $\nu_s$ around 1380 and 1280 cm$^{-1}$ respectively and the bending frequency aroud 830 cm$^{-1}$ (Table I). Lead and barium nitrites give spectra similar to those of alkali metal nitrites (Table I). Unlike ionic nitrites,

**Table I.** Major Infrared Absorption Bands (cm$^{-1}$) of Metal Nitrites [a]

| Compound | $\nu_a(NO_2)$ | $\nu_s(NO_2)$ | $\delta(ONO)$ |
|---|---|---|---|
| $NaNO_2$ | 1384 | 1270 | 828 |
| $KNO_2$ | 1384 | 1300 | 834 |
| $AgNO_2$ | 1365 | 1235 | 845 |
| $Ba(NO_2)_2$ | 1370 | 1250 | 820 |
| $Pb(NO_2)_2$ | 1360 | 1250 | 840 |
| $La(NO_2)_3$ | 1408, 1365, 1325 | 1250, 1175, 1030 | 845 |
| $Pr(NO_2)_3$[b] | 1475, 1365, 1325 | 1285, 1250, 1040 | 820 |
| $Nd(NO_2)_3$ | 1471, 1450, 1350, 1325 | 1253, 1205, 1042 | 815 |
| $Sm(NO_2)_3$ | 1470, 1365 | 1275, 1210, 1040 | 815 |
| $Dy(NO_2)_3$ | 1471, 1408, 1370 | 1266, 1035 | 815 |
| $Yb(NO_2)_3$ | 1481, 1460, 1345 | 1266, 1037 | 810 |
| $Ni(NO_2)_2$(8) | 1575, 1388, 1333 | 1240, 1080 | 830 |
| $CH_3NO_2$(7) | 1625 | ~840 | ~640 |

[a] The rare earth nitrites, particularly those of heavier rare earths, show bands to M-O vibrations in the 150-350 cm$^{-1}$ region. [b] Our frequencies do not agree with those reported in ref. 6.

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(a) Taken in part from the Ph.D. thesis of K.C.P. to be submitted to the Indian Institute of Technology, Kanpur, India.
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(1) J. R. Ferraro, *J. Mol. Spec.*, *4*, 99 (1960).
(2) J. R. Ferraro and A. Walker, *J. Chem. Phys.*, *42*, 1237 (1965); *ibid.*, *43*, 2689 (1965).
(3) (a) W. W. Wendlandt and J. L. Bear., *J. Inorg. Nucl. Chem.*, *12*, 276 (1960). (b) W. W. Wendlandt, *Anal. Chim. Acta.*, *15*, 435 (1956).
(4) F. Vratny and J. M. Honig, *Trans. Farad. Soc.*, *56*, 1051 (1960).
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(7) C. N. R. Rao, «Chemical Applications of Infrared Spectroscopy», Academic Press, New York (1963).
(8) C. C. Addison, B. R. G. Johnson, N. Logan and A. Wojcicki, *Proc. Chem. Soc.*, 306 (1961).

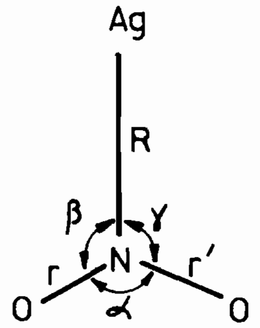
alkyl nitrites[7] exhibit two stretching bands at ~1620 and 820 $cm^{-1}$ due to the two N-O bonds of bond order ~2 and ~1 respectively. The separation between the two stretching vibration bands of metal nitrites can thus be an indirect measure of metal-oxygen interaction, just as the degree of disymmetry of the nitrate ion can be estimated by the spread between $\nu_4$ and $\nu_1$ of nitrates.[1]

Rare earth nitrites show a number of bands in the 1500-1300 and 1300-1000 $cm^{-1}$ regions as well as in the region 800-900 $cm^{-1}$ (Table I). The presence of high frequency bands in the region 1450-1500 $cm^{-1}$ is considered to be due to metal-oxygen interaction which tends to increase the bond order of one of the N-O bonds. It is interesting to note that anhydrous $Ni(NO_2)_2$[8], which is likely to have appreciable covalent character of the metal-oxygen bond shows three bands in the region of $\nu_a$ and two in the region of $\nu_s$, the highest frequency band being at 1575 $cm^{-1}$. The observation of a band in the 1000-1100 $cm^{-1}$ region in metal nitrites has been taken as an indication of metal-nitrito bonding.[9,10] All the rare earth nitrites show a fairly intense band in the 1000-1100 $cm^{-1}$ region just as $Ni(NO_2)_2$.

There appears to be little doubt that there is appreciable metal-oxygen bonding in anhydrous rare earth nitrites. Further, the presence of several bands in the N-O stretching region in rare earth nitrites indicates the complex structure of anhydrous nitrites. It was found that when hydrated metal nitrites were heated to 100-150°C (below the decomposition temperatures), a larger number of bands appeared in the N-O stretching region. Ferraro and Walker[2] have observed a number of bands in the $\nu_4$ and $\nu_1$ regions of anhydrous rare earth nitrates, some of which (on the high frequency side, > 1480 $cm^{-1}$) probably arise from N=O stretching.

Just as the anhydrous rare earth nitrates which show two bands (in the regions 180-215 and 220-270 $cm^{-1}$) due to metal-oxygen stretching vibrations, the heavier rare earth nitrites have also been found to show bands in the 150-350 $cm^{-1}$ region. These bands are also likely to arise from the metal-oxygen stretching vibrations. It is possible that the metal-oxygen bonding becomes stronger in the heavier metal nitrites just as in the corresponding nitrates.

*Normal Vibration Analysis of $AgNO_2$.* Silver nitrite[8,11] is known to be one of the few transition metal nitrites with some degree of covalency of the Ag-N bond. The crystal structure of $AgNO_2$ has been determined.[12] Normal vibrational analysis has been presently carried out for the in-plane vibrations of $AgNO_2$, employing the Urey-Bradley force field.[13] $AgNO_2$ was treated as a four atom system with $C_{2v}$ symmetry. The six vibrational modes may be categorised as $3A_1+1B_1+2B_2$ of which $3A_1$ and $2B_2$ are the in-plane modes. The internal coordinates of $AgNO_2$ are shown below:



The structural parameters and the symmetry coordinates for the in-plane vibrations are given in Table II. The calculated frequencies are compared with the observed values in Table III. It can be seen that the deviation is well below 2%. The infrared assignments in Table III confirm the presence of a fairly covalent Ag-N bond.

**Table II.** Symmetry Coordinates for the In-plane Vibrations and Structural Parameters of $AgNO_2$

| | $S_i$ | $S=UR$ | Vibrational mode | Abbreviation |
|---|---|---|---|---|
| *$A_1$ type* | $S_1$ | $(\Delta r+\Delta r')/\sqrt{2}$ | N-O sym. stretching | $\nu_s(NO)$ |
| | $S_2$ | $\Delta R$ | Ag-N stretching | $\nu(AgN)$ |
| | $S_3$ | $(2\Delta\alpha-\Delta\beta-\Delta\gamma)/\sqrt{6}$ | O-N-O bending | $\delta(ONO)$ |
| *$B_2$ type* | $S_4$ | $(\Delta r-\Delta r')/\sqrt{2}$ | N-O asym. stretching | $\nu_a(NO)$ |
| | $S_5$ | $(\Delta\beta-\Delta\gamma)/\sqrt{2}$ | Ag-N-O deformation | $\delta(AgNO)$ |

*Bond distances* :

$r = r' = 1.150$ Å; $R = 2.470$ Å [a]

*Bond angles* :

$\alpha = 128°$, $\beta = \gamma = 116°$[a]

*Force constants* : (md/Å)[b]

$K_{NO} = 6.200$ $H_{ONO} = 0.760$ $F_{O\ldots O} = 1.900$

$K_{AgN} = 2.400$ $H_{AgNO} = 0.050$ $F_{Ag\ldots O} = 0.060$

[a] Ref. 12. [b] Force constants are based on those of $AgNO_3$[26].

**Table III.** In-plane Vibration Frequencies of $AgNO_2$[a]

| ν ($cm^{-1}$) Calculated | ν ($cm^{-1}$) Observed[b] | Δ[c] | Assignements |
|---|---|---|---|
| 1369 | 1365 | 0.3 | $\nu_a(NO)$ |
| 1201 | 1235 | 2.8 | $\nu_s(NO)$ |
| 852 | 845 | 0.8 | $\delta(ONO)$ |
| 331 | 332 | 0.3 | $\nu(AgN)$ |
| 166 | — | — | $\delta(AgNO)$ |

[a] Spectra recorded in nujol mull. [b] $AgN^{15}O_2$ shows these bands at 1350, 1210, 840 and 327 $cm^{-1}$. [c] $\Delta = \frac{|\nu_{calc.} - \nu_{obs.}|}{\nu_{obs.}} \times 100$.

Apparently, $AgNO_2$ is akin to nitro compounds rather than nitrites. The assignments in Table III were further confirmed by recording the spectrum of $AgN^{15}O_2$. The Ag-N stretching bands in $AgN^{14}O_2$ and $AgN^{15}O_2$ confirm the assignments in Table III. It may be pointed out, however, that the band around 332 $cm^{-1}$ may have

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(9) R. B. Penland, T. J. Lane and J. V. Quagliano, *J. Am. Chem. Soc.*, *78*, 867 (1956).

(10) K. Nakamoto, J. Fujita and H. Marata, *J. Am. Chem. Soc.*, *80*, 4817 (1958).

(11) C. C. Addison and D. Sutton, *Inorg. Chem.*, *2*, 228 (1963).

(12) R. E. Long and R. E. Marsh, *Acta, Cryst.*, *15*, 448 (1962).

(13) T. Shimanouchi, *J. Chem. Phys.*, *25*, 35 (1955); *ibid.*, *17*, 245, 754, 848 (1949).

some contribution from the Ag . . . O stretching since two oxygens of the neighbouring nitrite group will be in the close vicinity of the Ag atom.[12] Further, a comparison between the frequencies calculated for a free molecule and those measured in the solid state can at best be only qualitative.

3. *Thermal Decomposition of Metal Nitrites.* Alkali nitrites are known to give rise to the oxide as the final product of decomposition. The decomposition is, however, supposed to proceed through the formation of nitrates as intermediates accompanied by the evolution of nitric oxide and nitrogen. The decomposition of alkali nitrites[14] may be considered to proceed through a series of interdependent reactions, some of the steps in the decomposition involving equilibrium reactions. It was therefore considered interesting to study the thermal decomposition of ionic nitrites, preferably under non-equilibrium conditions where the evolved gases would not interact with the solid residues. The decomposition of $NaNO_2$ could not be studied under vacuum since it can be distilled under reduced pressure ($\sim 5 \times 10^{-3}$ mm Hg) at 350-500°C.[15] The decomposition of barium and lead nitrites have been presently examined. Barium nitrite has been reported to show interesting stages in its thermal decomposition. According to Ray,[16] the mechanism of decomposition of $Ba(NO_2)_2$ is given by:

$$3Ba(NO_2)_2 \longrightarrow Ba(NO_3)_2 + 2BaO + 4NO \quad (1)$$

or

$$2Ba(NO_2)_2 \longrightarrow Ba(NO_3)_2 + BaO + NO + \tfrac{1}{2}N_2 \quad (2)$$

Of these, Ray preferred reaction (2). Recently, it has been reported[17] that the decomposition of $Ba(NO_2)_2$ also involves a series of interdependent reactions (arising from the equilibrium nature of some of the reactions) where the nitrate and nitrite are formed and decomposed successively. The thermogravimetric analysis (TGA) curve of $Ba(NO_2)_2$ recorded under vacuum ($\sim 3 \times 10^{-2}$ mm Hg) shows two distinct stages (Fig. 1).

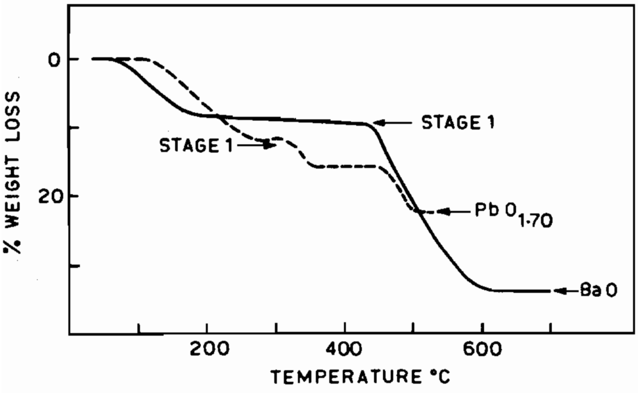

Figure 1. TGA curves of barium and lead nitrites.

The first stage of decomposition (initiation ~90°C and completion ~150°C) exactly corresponds to the stoichiometry given by reaction (2).[c] The nitrate formed by the reaction (2) apparently goes to the oxide directly (Fig. 1).

$$Ba(NO_3)_2 \longrightarrow BaO + 2NO_2 + \tfrac{1}{2}O_2 \quad (3)$$

In the TGA curve for the decomposition of lead nitrite (Fig. 1), the first stage of decomposition (initiation ~110°C and completion ~230°C) corresponds to reaction (4), the nitrate formed in this reaction further decomposing to $PbO_{1.7}$ in two stages[d] (~320°C and 450°C). It is not uncommon to obtain such non-stoichiometric oxides as decomposition products; praseodymium and terbium compounds as well as lead compounds are known to give rise to them.

$$3Pb(NO_2)_2 \longrightarrow Pb(NO_3)_2 + 2PbO + 4NO \quad (4)$$

Silver nitrite which is known to possess a fairly covalent Ag-N bond decomposes at a relatively low temperature (~120°C) to give silver metal and $NO_2$ gas. The kinetics of the decomposition of $AgNO_2$ follows the first order rate law (the rate constant at 140°C being $\sim 1.5 \times 10^{-2}$ $min^{-1}$) with an energy of activation of $\sim 6 \pm 2$ K.cal $mol^{-1}$.

Thermal decompositions of rare earth nitrites were investigated in detail by employing TGA (see Fig. 2 for typical TGA curves) and the various stages of

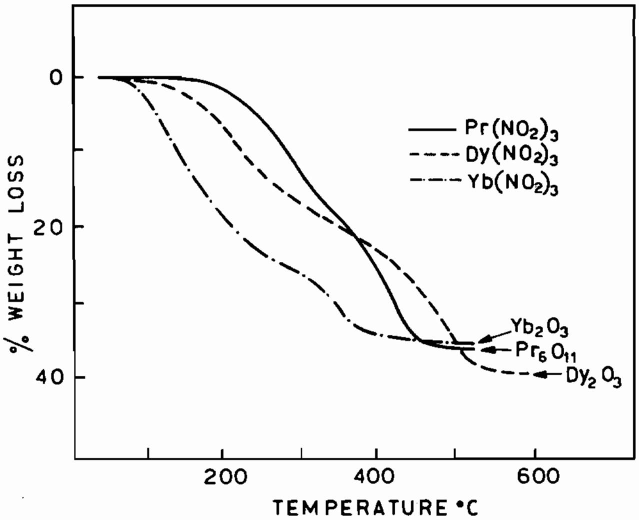

Figure 2. TGA curves of rare earth nitrites.

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(14) (a) M. C. Sneed and R. C. Brasted, «Comprehensive Inorganic Chemistry», VI, p. 131, D. Van Nostrand Company, Inc. Princeton, New Jersey (1957). (b) T. M. Oza and B. R. Walwalkar, *J. Indian Chem. Soc.*, *82*, 243 (1945).

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(17) T. M. Oza and J. C. Oza, *J. Indian. Chem. Soc.*, *43*, 759 (1966).

(c) The formation of NO in stage (1) was confirmed by trapping the gases evolved. The formation of the nitrate was established by recording the ultra-violet and infrared spectra of the residue just after the first stage of decomposition. The ultra-violet spectrum showed the ~ 305 mμ band characteristic of the nitrate ion.

(d) The stoichiometry for the stage at ~320°C corresponds to the formation of $Pb(NO_2)_2$, but it has not been possible to obtain clear evidence for the formation of the nitrite. In the literature, Vratny[5] has proposed the formation of $Pb(NO_2)_2$ as the intermediate in the thermal decomposition of $Pb(NO_3)_2$ on the basis of the i.r. spectra, but his data on the stoichiometry of the decomposition appear to contradict this proposal. If $Pb(NO_2)_2$ were the intermediate, NO gas should be one of the decomposition products and it is not observed. Further, $Pb(NO_2)_2$ decomposes at as low a temperature as 150°C and would be very unstable around 350°C.

decomposition are shown in Table IV. All the rare earth nitrites studied with the exception of $Pr(NO_2)_3$ seem to decompose according to the equation:

$$4Ln(NO_2)_3 \longrightarrow 2Ln_2O_3 + 12NO + 3O_2 \qquad (5)$$

where Ln stands for La, Nd, Sm, Dy or Yb. $Pr(NO_2)_3$ gives rise to $Pr_6O_{11}$ as the end product just as in the decomposition of other praseodymium compounds.[18-20]

**Table IV.** Thermal Decomposition of Rare Earth Nitrites

| | Initial temperature of decomposition, °C | Minimum oxide formation temp. °C |
|---|---|---|
| $La(NO_2)_3$ | 240 | 580 |
| $Pr(NO_2)_3$ | 220 | 450 |
| $Nd(NO_2)_3$ | 200 | 510 |
| $Sm(NO_2)_3$ | 200 | 500 |
| $Dy(NO_2)_3$ | 110 | 500 |
| $Yb(NO_2)_3$ | 90 | 350 |

All the rare earth nitrites start decomposing at considerably low temperatures. These temperatures are very much lower than those reported for the decomposition of nitrates.[e] The low temperatures of decomposition of the nitrites further lend support to the observation that rare earth nitrites are truely nitrites and not oxynitrates. Rare earth oxynitrates of the composition $LnONO_3$ are found to be the intermediates in the decomposition of nitrates as will be seen later. The low decomposition temperatures are indicative of the presence of some degree of covalency in the metal-oxygen bonds of rare earth nitrites (particularly in the case of heavier rare earth nitrites).

The kinetics of decomposition of three rare earth nitrites have been examined and the first order rate constants at only two temperatures are given below for the purpose of brevity. The values of the energies of activation, $E_a$, are also listed

| | Temp. (°C) | $k \times 10^3$ ($min^{-1}$) | $E_a$ ($K.cal\,mol^{-1}$) |
|---|---|---|---|
| $Nd(NO_2)_3$ | 240 | 3.72 | 1.8 ± 1 |
| | 290 | 4.34 | |
| $Dy(NO_2)_3$ | 280 | 0.46 | 3.8 ± 1 |
| | 380 | 0.78 | |
| $Yb(NO_2)_3$ | 210 | 0.23 | 1.3 ± 1 |
| | 280 | 0.28 | |

While it is difficult to comment on the variation of $E_a$ with the rare earth ion, the low energies of activation are suggestive of appreciable metal-oxygen interaction in the rare earth nitrites.

4. *Thermal Decomposition of Metal Nitrates.* Simple ionic nitrates such as potassium nitrate decompose to the nitrite and oxygen. Silver and lead nitrates, on the otherhand, decompose readily to give $NO_2$, oxygen and the metal or the oxide as the products of decomposition. The kinetic studies of the decomposition of silver nitrate showed that there was induction time at lower temperatures (~1 hr. at 450°C) which decreased with increasing temperature. At relatively high temperatures or beyond the induction period, the kinetic data obeyed the first order rate law (rate constant at 520°C, $\sim 2.2 \times 10^{-2}$ $min^{-1}$) with an $E_a$ of $\sim 14 \pm 2$ $K.cal\ mol^{-1}$.

The TGA curve for the decomposition of lead nitrate showed only one stage around 230°C and the final product of decomposition was the non-stoichiometric lead oxide $PbO_{1.4}$. This is in variance with the observation of Vratny and Gugliotta[5] who noticed no significant oxidation of $Pb^{2+}$ ion in the decomposition of $Pb(NO_3)_2$; however, they have not reported the actual composition of the end products. The rate curves for the decomposition of $Pb(NO_3)_2$ showed that the decomposition was rapid in the initial stages and becomes slow at later stages. The rate data for the initial as well as the final stages of decomposition could be fitted into the first order rate law, and rate constants at a few temperatures are given below:

| Temp. °C | Rate constants ($min^{-1}$) for the Initial stage | Final stage |
|---|---|---|
| 265 | $8.68 \times 10^{-4}$ | — |
| 280 | $2.23 \times 10^{-3}$ | $2.83 \times 10^{-4}$ |
| 300 | — | $1.38 \times 10^{-3}$ |
| 310 | $1.56 \times 10^{-2}$ | $2.55 \times 10^{-3}$ |

The energies of activation were found to be ~37 and ~45 $K.cal\ mol^{-1}$ respectively for these two stages.[f] These values of $E_a$ differ from those reported[21] recently from the gasometric determination of the kinetics where the $E_a$ values for the initial and later stages were found to be ~60 and ~11 $K.cal\ mol^{-1}$ respectively. The average activation energy for the decomposition of $Pb(NO_3)_2$ calculated from the TGA data[22] was found to be 57 $K.cal\ mol^{-1}$, a value comparable to the values of $E_a$ obtained from the kinetic data.

Unlike the decomposition of simple ionic nitrates, the decompositions of rare earth nitrates are found to be much more complex. It has been reported on the basis of TGA studies of hydrated rare earth nitrates, that the formation of anhydrous nitrates is clearly indicated only in the lighter rare earths (La to Nd).[3] Further, all the rare earth nitrates with the exception of Yb and Lu are known to show a stage in the decomposition corresponding to the formation of $LnONO_3$, the stability of which is lower in heavier rare earths. Vratny and coworkers[4,6] have proposed bridged nitrites as intermediates in the decomposition of praseodymium and a few other nitrates.

When the TGA curves of rare earth nitrates were recorded carefully, it was found that most of the hydrated rare earth nitrates show the formation of the anhydrous nitrate as a definite stage in the decomposition (Fig. 3) contrary to the observations of

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(e) The thermal decomposition of rare earth nitrates are discussed later in this paper and the minimum oxide formation temperatures in the case of nitrates are found to be considerably higher (Table V). It is, however, not clear at present why the TGA curves of rare earth nitrites (Fig. 2) show shoulders at intermediate temperatures.

(18) K. C. Patil, G. V. Chandrashekhar, M. V. George and C. N. R. Rao, *Canadian J. Chem.*, in print.

(19) R. L. N. Sastry, S. R. Yoganarasimhan, P. N. Mehrotra and C. N. R. Rao, *J. Inorg. Nucl. Chem.*, *28*, 1165 (1966).

(20) W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, *7*, 51 (1958).

(f) The uncertainy in these values are likely to be large (~20%).

(21) S. R. Mohanty and M. N. Ray, *Inorg. Nucl. Chem. Letters*, *2*, 387 (1966).

(22) N. G. Dave and S. K. Chopra, *Z. Physik. Chem.*, *48*, 257 (1966).

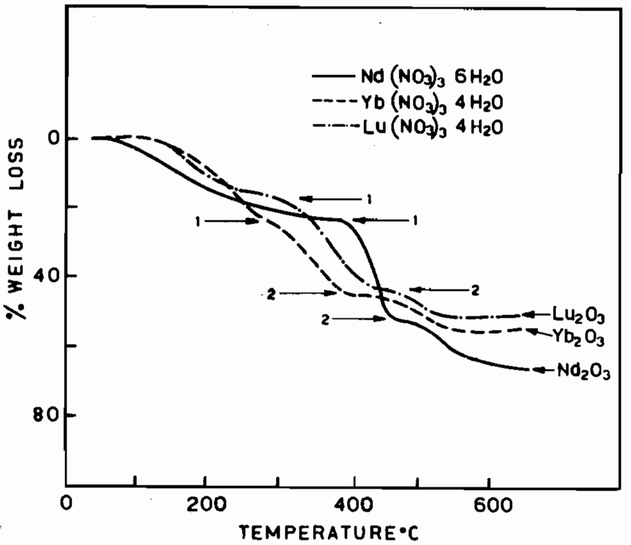

Figure 3. TGA curves of rare earth nitrates: Stage (1) $Ln(NO_3)_3$; Stage (2) $LnONO_3$.

Wendlandt.[3] All the rare earth nitrates show evidence for the formation of the so-called oxynitrate phase of the composition $LnONO_3$, although the temperature range of stability is smaller in the case of Yb and Lu. The minimum oxide ($Ln_2O_3$) formation temperature ($T_o$) decreases as one goes down the rare earth series. The values of $T_o$ in the case of Yb and Lu are 500°C and 470°C respectively compared to 730°C in the case of La. The results confirm the increase in M-O covalency down the series[2] (Table V).

**Table V.** Thermal Decomposition of Rare Earth Nitrates

| | Stability range of anhyd. nitrate (°C) | Stability range of $LnONO_3$ (°C) | Min. oxide formation temp. (°C) |
|---|---|---|---|
| $La(NO_3)_3 . 6H_2O$ | 240-420 | 515-575 | 730 |
| $Nd(NO_3)_3 . 6H_2O$ | 280-350 | 460-500 | 650 |
| $Dy(NO_3)_3 . 4H_2O$ | 260-280 | 420-440 | 630 |
| $Yb(NO_3)_3 . 4H_2O$ | 260-270 | 340-400 | 500 |
| $Lu(NO_3)_3 . 4H_2O$ | 220-230 | 370-390 | 470 |

The stable composition $LnONO_3$ which is found in the decomposition of the rare earth nitrates is similar to the intermediates $LnO . ½CO_3$ and $LnO . ½SO_4$ found in the decompositions of rare earth carbonates[19] and sulphates.[20] It is interesting that the composition $LnOY(Y{=}NO_3^-$, ½ $CO_3^=$ or ½ $SO_4^=)$ is formed as the stable intermediate in the thermal decomposition of all these rare earth salts, but the reason for this is not clear. In nitrate decompositions, there appears to be no alternative way of satisfactorily representing this stable intermediate phase other than assigning the oxynitrate structure, $LnONO_3$. For example, the stoichiometry precludes the formation of ionic or bridged nitrites as intermediates.[g]

From the preceeding discussion it becomes clear that $LnONO_3$ is a stable intermediate. As such, the proposal of Vratny and coworkers[4,6] that nitrites are formed as intermediates in the decomposition of rare earth nitrates does not seem to be valid. The conclusion of Vratny and coworkers were mainly based on the observation of some common bands in the infrared spectra of partially decomposed nitrates and nitrito-complexes[23,24] or metal nitrites.[6] The infrared spectra of several rare earth nitrates[h] partially decomposed up to the $LnONO_3$ stage have been presently examined. The positions of the major infrared bands of $LnONO_3$ are shown in Table VI. The band positions and their relative intensities do not compare well with those of anhydrous rare earth nitrates or with the data on nitrites (Table I). For example, while all the rare earth nitrites show an intense band around 1250 cm$^{-1}$, the $LnONO_3$ compositions show a band around 1200 cm$^{-1}$. The 1200 cm$^{-1}$ band increases in intensity as the nitrate is heated and the intense band persists up to temperatures appreciably higher than the decomposition temperatures of the nitrites. The 1200 cm$^{-1}$ band was, however, absent in the case of the partially decomposed nitrates of Yb and Lu where the $LnONO_3$ composition has limited stability. It is felt that all the observed bands of $LnONO_3$ compositions arise from a nitrate group which is strongly coordinated.

The electronic absorption spectra of the nitrate, the nitrite and the oxynitrate of dysprosium and neodymium recorded in the form of pellets, showed that the spectra

**Table VI.** Infrared Bands of Rare Earth Oxynitrates Obtained as Intermediates in the Decomposition of Nitrates*

| Compound | $\nu_4$ | $\nu_1$ | $\nu_2$ | $\nu_6$ |
|---|---|---|---|---|
| $LaONO_3$ | 1600, 1449 | 1365, 1333, 1308, 1206 | 1030 | 818, 707 |
| $PrONO_3$ | 1460, 1445 | 1365, 1340, 1200 | 1030 | 830 |
| $NdONO_3$ | 1449 | 1368, 1317, 1200 | 1025 | 821, 710 |
| $DyONO_3$ | 1470 | 1370, 1310, 1190 | 1030 | 819 |
| $YbONO_3$ | 1479, 1439 | 1370, 1282 | 1020 | 816 |
| $LuONO_3$ | 1450, 1408 | 1353, 1325, 1299 | 1042, 1028 | 891, 877, 847, 801, 762, 729 |

* The nomenclature of the bands is similar to that of Ferraro and Walker[2] in the case of nitrates. It is not possible to ascribe the bands in the $\nu_1$ and $\nu_2$ regions to the so-called Metal-Oxygen vibrations proposed by Barraclough, Lewis and Nyholm, *J. Chem. Soc.*, 3552 (1959).

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[g] It should be noted that rare earth nitrites decompose at considerably lower temperatures than the rare earth nitrates (Table IV & V). The $LnONO_3$ compositions are stable at temperatures much higher than the decomposition temperatures of nitrites and in some cases the $LnONO_3$ formation temperatures are higher than the minimum oxide temperatures. Further, NO (which should have been one of the decomposition products, if nitrites were present) was not found.

[h] Infrared spectra of anhydrous rare earth nitrates recorded in this laboratory agree well with those reported by Ferraro and Walker.[2]

(23) B. M. Gatehouse, *J. Inorg. Nucl. Chem.*, *8*, 79 (1958).

(24) D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 3, 1389 (1964).

of $LnONO_3$ corresponded closely to those of the nitrates rather than of the nitrites.[i] Since there is not much evidence for the presence of ionic nitrate groups even in the lighter rare earth nitrates[2] such as $Pr(NO_3)_3$, it is not surprising that in $LnONO_3$ the nitrate group should be much more strongly coordinated. On the basis of the preceeding discussion it appears that in $LnONO_3$ there may be an unique coordination of nitrate.[1]

The kinetics of decomposition of three rare earth nitrates were also examined and the first order rate constants for only two temperatures are given below for the sake of brevity.

| | Temp. (°C) | $k \times 10^3$ (min$^{-1}$) | $E_a$ (K.cal mol$^{-1}$) |
|---|---|---|---|
| $Nd(NO_3)_3$ | 390 | 0.57 | 8 |
| | 430 | 0.81 | |
| $Dy(NO_3)_3$ | 310 | 0.25 | 5.5 |
| | 360 | 0.37 | |
| $Yb(NO_3)_3$ | 290 | 2.00 | 11 |
| | 325 | 3.60 | |

Just as in the case of nitrites, there does not seem to be any simple variation of activation energy with the rare earth ion. The $E_a$ values are, however, appreciably larger than those for the decomposition of nitrites.

## Experimental Section

Barium and lead nitrites were prepared by the reaction of the respective chlorides with silver nitrite. $AgN^{15}O_2$ was prepared by the reaction of $KN^{15}O_2$ (with 96.4% $N^{15}$, Isomet Corporation, U.S.A.) with $AgNO_3$. All the rare earth nitrites were prepared by the reaction of respective chlorides with $AgNO_2$. The compounds were then dried over $P_2O_5$ under vacuum and heated to 100°C. The resulting compounds were found to be anhydrous as found by elemental as well as thermogravimetric analyses.

Infrared spectra were recorded in the 4000-250 cm$^{-1}$ region employing a Carl-Zeiss UR-10 spectrometer (with LiF, NaCl and KBr prisms) as well as a Perkin-Elmer Model 521 double-grating spectrometer. Spectra below 250 cm$^{-1}$ were recorded for us by Perkin-Elmer Corp. and Beckman Instruments Inc., to whom thanks aer due. Samples were prepared as KBr pellets and mulls in nujol or fluorolube. The spectra of anhydrous rare earth nitrites were recorded after heating them to different temperatures in the range 100°-150°C. The spectra or rare earth nitrates were recorded in the anhydrous stage (as found in TGA analyses) and also after heating them up to the stage $LnONO_3$ (Ln = rare earth). The infrared spectra of barium and lead nitrites were recorded after heating them up to 200°C and 250°C respectively in order to find evidence for the formation of nitrates as intermediates. The course of decomposition of $AgNO_3$, $Pb(NO_3)_2$ as well as rare earth nitrates was followed by taking the spectra of the samples heated for different periods at various temperatures.

The electronic spectra were recorded by emplowing a Cary-14 spectrometer. Samples were prepared as KBr pellets in many instances. Some of the spectra were also recorded in aqueous solutions.

An IBM 1620 digital computer was used for the normal vibration calculations of $AgNO_2$.

Thermogravimetric analysis (TGA) curves were recorded by employing an Aminco thermobalance fitted with an X-Y recorder, a furnace operated by a temperature programmer, precision spring and a quartz reaction chamber which was hooked on to a vacuum line. In this apparatus, the decompositions could be studied in air or vacuum. The TGA curves for all nitrites and nitrates studied presently were in vacuum ($\sim 3 \times 10^{-2}$ mm Hg).

The kinetics of decomposition were examined by recording the weight loss curve as a function of time at a constant temperature; the kinetics were studied at several temperatures. In the case of the thermal decompositions of $AgNO_3$ and $AgNO_2$, however, the kinetics of decomposition were followed by the estimation of Ag° residue as well as by infrared spectroscopy.

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(i) In solution of dil. HCl, however, the $LnONO_3$ compounds gave bands due to nitrites as well as nitrates. This is possibly due to the cleavage of the bond (b) as shown by Addison[25] in beryllium nitrate. $M^aO^bNO_2 \rightarrow M{-}O. + NO_2$.

(1) For example, one can write structures with rare earth ions forming $LnO_6$ octahedra where the oxygens from the nitrate as well as the oxide ions are shared by more than one octahedron.

(25) C. C. Addison and A. Walker, *J. Chem. Soc.*, 1220 (1963).

(26) S. C. Wait Jr. and A. T. Ward, *J. Chem. Phys.*, *44*, 448 (1966).