

## Note

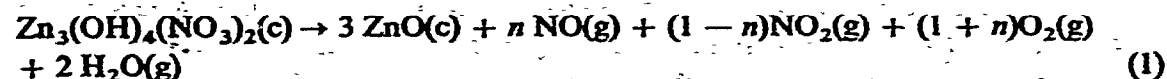
### A calorimetric study of the thermal decomposition of zinc hydroxynitrate $Zn_3(OH)_4(NO_3)_2$

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(Received 18 February 1977)

The thermal decomposition of zinc hydroxynitrates  $Zn_3(OH)_4(NO_3)_2$  and  $Zn_3(OH)_8(NO_3)_2$  has been reported by several authors<sup>1–3</sup>, who have proposed a reaction scheme in which nitrogen oxides are liberated from the destruction of the nitrate group. Thus, for the first hydroxy salt the reaction can be written as follows:



with  $0 \leq n \leq 2$ .

In connection with a general study on the process of zinc hydroxynitrates transformations, we have found it necessary to re-examine this reaction scheme by comparing the enthalpy change  $\Delta H_1^\circ$  found from calorimetric studies with that calculated from enthalpies of formation of the different products in eqn (1).

Recently, we have reported<sup>4</sup> the value of  $-442,410 \text{ cal mol}^{-1}$  for the enthalpy of formation of  $Zn_3(OH)_4(NO_3)_2$ . This result used in conjunction with the values reported in the literature<sup>5, 6</sup> for products of reaction (1) gives a theoretical value for the enthalpy of decomposition  $\Delta H_1^\circ$  between  $91,390$  and  $118,670 \text{ cal mol}^{-1}$  depending on the value of  $n$  used.

#### EXPERIMENTAL

Zinc hydroxynitrate  $Zn_3(OH)_4(NO_3)_2$  was obtained in the crystalline form by slowly evaporating a solution of zinc nitrate hexahydrate ("Baker Analysed Reagent") melted at  $120^\circ\text{C}$ <sup>7</sup>.

The calorimeter measurements were determined on samples whose masses were between 10 and 210 mg using a Calvet microcalorimeter. The microcalorimeter was calibrated electrically by the Joule effect during the decomposition of the hydroxy salt using linear heating rates of either  $6$  or  $2^\circ\text{C h}^{-1}$ . The experiments were carried

out either in a vacuum which was maintained at  $10^{-2}$  Torr, or in a dry nitrogen stream flowing at the rate of  $50 \text{ ml min}^{-1}$ .

## RESULTS AND DISCUSSION

Table 1 gives the experimental results for the heat of decomposition  $\Delta H_1^\circ$  for  $\text{Zn}_3(\text{OH})_4(\text{NO}_3)_2$ . These values are inferior to that calculated above, and are dependent on the mass of the sample when the pyrolysis are carried out in nitrogen stream.

This disagreement implies that the reaction scheme (1) is incorrect and leads us to suggest that the decomposition of the hydroxy salt occurs according to the following equation where the nitrate groups are not decomposed:



The enthalpy change for this reaction, calculated from the enthalpies of formation, is  $\Delta H_2^\circ = 68,770 \text{ cal mol}^{-1}$ . This result is very close to the mean value,  $67,650 \pm 700 \text{ cal mol}^{-1}$ , obtained from the decomposition carried out under vacuum, taking into account experimental errors and the fact that we have ignored the variation of the specific heat in the experimental temperature range  $25\text{--}270^\circ\text{C}$ . The agreement is also good for runs 9 and 10. Moreover, the formation of nitric acid has been confirmed by mass spectral analysis of the gas appearing during the reaction.

The larger experimental values obtained (runs 6, 7, 8) when the reaction was performed under a nitrogen stream with larger sample masses can be explained by interfering secondary reactions. Pannetier and Djega-Mariadassou<sup>1, 2</sup> have show experimentally the formation of nitrogen oxides when the decomposition occurs in nitrogen or helium stream. We have observed the same results by mass spectral analysis of the gases leaving the calorimeter. Nitrogen dioxide results from the decom-

TABLE 1

EXPERIMENTAL RESULTS FOR THE HEAT OF DECOMPOSITION OF HYDROXYNITRATE  $\text{Zn}_3(\text{OH})_4(\text{NO}_3)_2$

<i>Expt. No.</i>	<i>Heating rate (<math>^\circ\text{C h}^{-1}</math>)</i>	<i>Atmosphere</i>	<i>Sample mass (mg)</i>	$\Delta H_1^\circ$ ( <i>cal mol<sup>-2</sup></i> )
1	6	vacuum	51.9	67270
2	6	vacuum	207.5	68470
3	6	vacuum	198.2	67140
4	6	vacuum	55.9 <sup>a</sup>	68100
5	2	vacuum	13.25 <sup>a</sup>	67280
6	6	N <sub>2</sub>	192.6	72910
7	6	N <sub>2</sub>	198.6	75660
8	6	N <sub>2</sub>	209.15	75360
9	6	N <sub>2</sub>	54.25 <sup>a</sup>	69950
10	2	N <sub>2</sub>	13.95 <sup>a</sup>	67750

<sup>a</sup> These samples are very finely ground and deposited thinly on the walls of the sample holder.

position of gaseous nitric acid. The mechanism and kinetics for this reaction have been studied by several authors<sup>8-12</sup>. The overall reaction is



Nitrogen dioxide can also decompose above 200°C<sup>13</sup> according to the reaction



The corresponding heats of reaction are  $\Delta H_3^\circ = 11,312 \text{ cal mol}^{-1}$  and  $\Delta H_4^\circ = 13,640 \text{ cal mol}^{-1}$ , respectively.

The secondary reactions are less likely to occur in the dynamic vacuum since reaction (2) occurs in a lower temperature range 110–200°C and the nitric acid is evacuated continuously and, therefore, has a lower pressure. On the other hand, they can occur when the experiments are carried out under nitrogen since reaction (2) occurs at a higher temperature 170–250°C and also for runs 6, 7 and 8 increased sample thickness (about 3 mm) caused by the larger sample mass could cause a partial pressure of nitric acid inside the sample greater than 1 Torr due to the difference of density between HNO<sub>3</sub> and N<sub>2</sub> gases. Therefore, the nitric acid could remain in the sample holder for sufficient time to partially decompose, eventually catalysed by the finely divided ZnO formed during the pyrolysis. Runs 9 and 10 show that the importance of the secondary reactions are minimized when the sample mass is kept to a minimum.

#### CONCLUSION

In contrast to the conclusions drawn by other workers, this study shows that the zinc hydroxynitrate decomposes according to the eqn (2). It is interesting to note the analogies that exist between the structural characteristics on one hand, and the thermal decomposition on the other, for zinc hydroxynitrate and bivalent metal hydroxides of the brucite type. In effect, the hydroxy salt Zn<sub>3</sub>(OH)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> is a structural derivative of the brucite type having one hydroxyl ion in three replaced by an oxygen atom of the nitrate group<sup>14, 15</sup>. This substitution causes an increase in the interlayer spacing. The thermal decomposition of the hydroxides of the brucite type liberates a molecule of water<sup>16, 17</sup>, and logically we have noted that the zinc hydroxynitrate decomposes thermally liberating free molecules of water and nitric acid. We think that the thermolysis of other hydroxynitrates will follow a similar mechanism.

Lastly, this study is an example of the use of calorimetric measurements of heats of reaction to decide which of several proposed reaction paths is correct.

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