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# THE MASS SPECTROMETRIC AND THERMOGRAVIMETRIC DETERMINATION OF RISING TEMPERATURE KINETIC PARAMETERS FOR THE SOLID STATE DECOMPOSITION OF NICKEL NITRATE HEXAHYDRATE

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## ABSTRACT

Rising temperature kinetic parameters have been obtained for the solid state decomposition of nickel nitrate hexahydrate in vacuo. The decomposition was followed by normal thermogravimetric analysis (TG), an evolved gas analysis (EGA) system, and by differential thermal analysis (DTA). The EGA system used is a development of a mass spectrometric system employing a large expansion bulb to reduce pressure rises and minimal gas removal. An integral method of calculating the kinetic parameters was used.

The decomposition of nickel nitrate hexahydrate was found to begin at 315 K, the only product of any significance being water up to 400 K; thereafter water and nitric oxide/dioxide were evolved. The rate controlling steps, considering both kinetic and theoretical thermodynamic data, are diffusion controlled for the main nitrate decomposition. Evolution of nitric oxide/dioxide occurred in three rate determined stages. The first occurred over the range $\alpha = 0.0–0.073$ and was thought to correspond to hydrolysis of the nitrate. The remaining two stages had Arrhenius kinetic parameters of $E = 160.3$ kJ mole$^{-1}$, $A = 2.50 \times 10^{11}$ s$^{-1}$ and $E = 53.5$ kJ mole$^{-1}$, $A = 5.90 \times 10^{1}$ s$^{-1}$ for the ranges $\alpha = 0.073–0.425$ and $\alpha = 0.425–0.993$, respectively, where $E$ is the activation energy and $A$ is a pre-exponential term.

## INTRODUCTION

The kinetics of the thermal decomposition of solids are normally calculated from measurements of the change in a physical property, such as mass, associated with a change in temperature. However, it has long been recognised that such measurements are often a combination of physical processes such as sublimation, evaporation, dehydration and decomposition as well as a combination of differing chemical processes. In this study the thermal decomposition is studied using a vacuum microbalance, an evolved gas analysis (EGA) system based on a mass spectrometer, together with a differential thermal analysis (DTA) system.

The EGA system is based on a method developed by Dollimore and co-workers [1–3] for desorption studies on graphite. This consisted of a mass spectrometer linked to a vacuum microbalance via an expansion bulb. It was shown that the results from the mass spectrometer were in excellent agreement with those obtained from the microbalance. Each run was begun with the microbalance at a pressure of $10^{-6}$ Torr, rising to a predetermined pressure of up to 20 Torr. Mass spectrometric measurements were made either via a calibrated slow leak valve or via an oil diffusion pump evacuating the microbalance chamber into an expansion bulb. Both of these methods suffer from drawbacks, however. Firstly, the effect of gas sampling from the system, for the purposes of a kinetic study, must be either to remove all the product(s) as it is formed or to remove a negligible amount. Anything in between requires very complex mathematical treatment to allow for gas flow rates through a sampling valve or capillary at varying pressures and diffusion coefficients. Secondly, the use of a diffusion pump to remove all products from the sample requires the absence of any secondary reactions due to either the thermal instability of any evolved gases or breakdown of the diffusion pump liquid with corrosive evolved gases. Thus this study uses a gas sampling system of negligible gas removal.

Previous studies of the thermal decomposition of nickel nitrate hexahydrate have shown the reaction to be complex. Weigel et al. [4,5] have studied the decomposition at a variety of heating rates using a calorimeter and found, depending on the conditions used, evidence for the following species:

| | |
|---|---|
| nickel nitrate hexahydrate (reactant) | $Ni(NO_3)_2 \cdot 6\,H_2O$ |
| nickel nitrate tetrahydrate | $Ni(NO_3)_2 \cdot 4\,H_2O$ |
| nickel nitrate dihydrate | $Ni(NO_3)_2 \cdot 2\,H_2O$ |
| nickel nitrate (anhydrous) | $Ni(NO_3)_2$ |
| basic nickel nitrate | $Ni(NO_3)_2 \cdot 2\,Ni(OH)_2$ |
| nickel oxide (product) | NiO |

Prost and Robin [6] found that under vacuum ($10^{-2}$ Torr) two stages of the dehydration could be observed under isothermal conditions, the first having an activation energy of 99.5 kJ mole$^{-1}$ and the second 122.6 kJ mole$^{-1}$. The first stage was found to have an order of 2/3 whilst the second had an order of approximately 1.6.

The aim of this study is to calculate the Arrhenius parameters for the thermal decomposition of nickel nitrate hexahydrate, calculated from TG and EGA studies, using DTA of both nickel nitrate and nickel hydroxide to supplement the data.

## EXPERIMENTAL

### *Equipment and materials*

For the EGA study the instrument used was an AEI MS10 mass spectrometer — a single focussing, 180° deflection instrument with a 2 inch ion radius. This was connected via a slow leak sinter, through an expansion bulb (~ 2 l) to a previously evacuated quartz sample tube which was heated by a furnace controlled by a Stanton Redcroft Linear Temperature Programmer Mk. 3 at a constant heating rate of 0.8°C min$^{-1}$ ± 0.1°C. Temperature control utilised a thermocouple placed in thermal contact with the sample tube outer wall, temperature measurement being by a thermocouple placed in a 'dimple' in the base of the sample tube. The pressure in the system was measured at $10^{-6}$ Torr at the beginning of the experiment, rising to $10^{-2}$ Torr at the end. Gas loss into the mass spectrometer due to the continuous sampling system was found to be negligible over a 10 h period.

Using equilibrium data, Stern [7] has shown that any study of nitrate decomposition products need only to look at $NO_2$ and NO evolution. Although other nitrogen oxides may be formed, these have relative short life times. The equilibrium $NO + 0.5\ O_2 = NO_2$ is very temperature dependent, $NO_2$ being predominant up to 500 K. However, preliminary studies showed that $NO_2$ cracked on the mass spectrometer filament to give a peak at $m/e = 30$. Thus, since the majority of the system was at room temperature, the total evolution of nitrogen from the sample could be followed by measuring the peak at $m/e = 30$. Since the peak height is thus proportional to $\alpha$, the fractional decomposition of the reactant, then a graph of $\alpha$ vs. temperature $T$, can be constructed directly from the output data of the instrument.

The vacuum microbalance system consisted of a CI Electronics balance linked to a vacuum manifold capable of being pumped down to $10^{-6}$ Torr using a mercury diffusion pump backed by a single rotary pump. Heating was achieved using the same furnace and temperature control as that used in the EGA system, operating at the same heating rate. Temperature measurement was via a thermocouple placed 1 mm below the glass sample crucible, the leads being drawn out through a glass/metal seal in the bottom of the balance hangdown tube. Due to the nature of the system the pressure was maintained at $10^{-6}$ Torr during an experiment.

DTA was achieved using a Stanton Redcroft 671 unit. This is a low furnace mass instrument allowing heating rates of 1–20°C $min^{-1}$, with a cut-out switch at 500°C, measuring the temperature with an accuracy of ±0.1°C. The DTA signal is derived from thermocouples welded to two small metal platforms upon which rest the sample and reference crucibles. During each experiment the pressure inside the furnace was maintained at $10^{-2}$ Torr using a two stage rotary pump, the heating rate being 1.0°C $min^{-1}$.

The chemicals used were reagent grade nickel nitrate hexahydrate and nickel hydroxide. Sample weights of approximately 5 mg were used in each experiment. One hour was allowed for sample degassing under the vacuum conditions described earlier.

### *Method*

The method of calculating the kinetic parameters was an integral method based on the following equation [8]

$$\ln g(\alpha) - \ln p_n(x) = \ln\left[\frac{A_n E^{n+1}}{R^{n+1}\beta}\right] \tag{1}$$

where $g(\alpha)$ is a functional form of $\alpha$ representing the mechanism, $p_n(x)$ is the temperature integral $\int_x^{x_0} x^{-(n+2)} \exp(-x)\, dx$ where $x = E/RT$, $A_n$ is the pre-exponential factor, $R$ is the gas constant, $E$ is the activation energy, $\beta$ is the heating rate and $n$ is a constant. A computer program has been written [9] to calculate $A_n$ and $E$ for the case where $n = 0$, i.e. assuming a pre-exponential function $A = A_0 T^0$. The activation energy was calculated to an accuracy of ±0.3 kJ mole$^{-1}$. The approximation to the temperature integral was based on the Schloemilch series and truncated after the fourth term

$$p_0(x) = \frac{e^{-x}}{x^2}\left[1 - \frac{2}{x+1} + \frac{4}{(x+1)(x+2)} - \frac{10}{(x+1)(x+2)(x+3)}\right] \qquad (2)$$

Twenty-six functions of $\alpha$ were considered, these being derived from two sources [10,11] assuming the differential form of the rate equation to be correct [12]. The program plotted ln g($\alpha$) vs. $1/T$ for each g($\alpha$), these plots being used to determine the regions of linearity. The values of $A$ and $E$ were then calculated on the basis of these regions for each function of $\alpha$.

Although the selection of g($\alpha$) can be successfully made by consideration of the value of $A$, the standard deviation of each plot, and the probability of certain processes occurring [9,13], this method is capable of improvement. The method used in this work is based on the following arguments.

The most commonly used technique of measuring the slope and standard deviation or error in ln g($\alpha$) vs. $1/T$ or, in the differential methods, ln $k$ vs. $1/T$ plots, is by the method of least squares. This method, however, assumes that for any set of data points, $y_i$ vs. $x_i$, the error in the independent variable $x$ is negligible compared with that in the dependent variable $y$. In thermal analysis where $x$ is some function of temperature and $y$ is a function of $\alpha$ this is true, thus enabling comparisons to be made between different conditions, samples, etc. However, in the comparison of different functions of $\alpha$ for the same set of $\alpha$–$T$ data, then ln g($\alpha$) or ln $k$ are the independent variables and so the standard deviation in the $x$ direction must be used. In practice, with data containing very little error, such as that obtained theoretically, then the difference in selecting the correct function from the two possible standard deviations will not be noticed. The drawback of using the standard deviation in the $x$ direction is that functions of the type $[-\ln(1-\alpha)]^n$ or $\alpha^n$ become analytically indistinguishable. Error in the $y$ direction is simply magnified as $n$ increases, with the standard deviation in the $x$ direction remaining constant. Different values of $n$ can only be distinguished through consideration of $A$ and other complementary data [14].

## RESULTS AND DISCUSSION

Figure 1 shows the $\alpha$–$T$ curves derived from the TG (a) and EGA (b) systems together with the DTA traces for nickel nitrate hexahydrate (c′) and nickel hydroxide (c″). Curve (d) is the $\alpha$–$T$ trace for the final section of the TG curve only. From direct visual observation through the viewing port in the DTA instrument, peak A

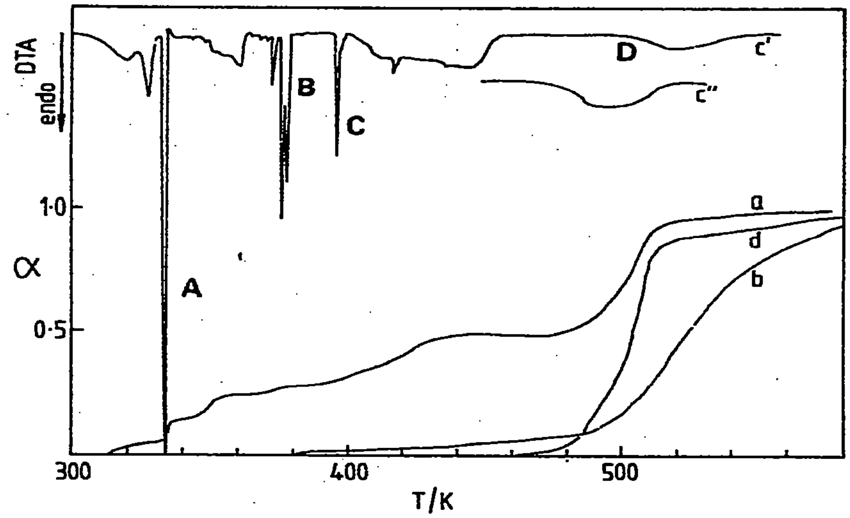

Fig. 1. Plots of the fractional decomposition ($\alpha$) vs. temperature ($T$) derived from the TG (a) and EGA (b) systems together with the DTA traces for nickel nitrate hexahydrate (c′) and nickel hydroxide (c″). Curve (d) is the $\alpha$–$T$ trace for the final section of the TG curve only.

on the DTA trace for the nitrate (c′) corresponds to the sample partially dissolving in its own water of crystallisation; peak B being due to the subsequent recrystallisation. Both the DTA and TG traces show that the process of dehydration is complex and multistaged. In general, the traces agree with each other although there are a number of significant differences which are discussed below.

As can be seen from Fig. 1 comparing traces (a) and (b) the EGA trace for total nitrogen evolution does not correspond in shape to the TG curve. Nitric oxide/dioxide evolution begins at approximately 400 K, accelerating up to $\alpha = 0.25$, $T = 508$ K and, from there, steadily decelerates. The TG curve begins at 460 K, accelerating up to approximately $\alpha = 0.6$, $T = 505$ K and, from there steadily decelerates until $\alpha = 0.86$, $T = 515$ K when a long decay period occurs up until $\alpha = 1.0$, $T = 605$ K. Peak D on the DTA trace for pure nickel nitrate hexahydrate corresponds almost exactly with the main part of the EGA curve ($\alpha = 0.19$–$0.82$) whilst the trace for pure nickel hydroxide corresponds with the TG curve ($\alpha = 0.05$–$0.92$). These observations suggest that the initial evolution of $NO/NO_2$ was due to hydrolysis of the nitrate by water vapour as suggested by Weigel et al. [4,5]. Indeed, visual observations showed that the nitrate remained green up to a temperature of 450 K, indicating the existence of a hydrated form of nickel, and gradually blackened until approximately 495 K. The absence of a peak on the DTA trace c′ corresponding to the loss of water in the range $\alpha = 0.05$–$0.92$ for the TG trace is discussed later.

The plots of ln g($\alpha$) vs. $1/T$ for the EGA date (Fig. 2) showed the presence of three distinct regions $\alpha = 0$–$0.073$, $0.073$–$0.425$, $0.425$–$0.993$. The standard deviations for each function of $\alpha$ over each region were calculated as described. Selection of the lowest standard deviation gave the results shown in Table 1 with the

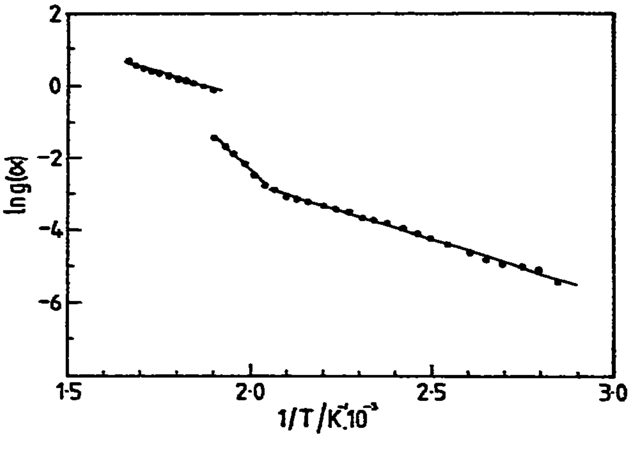

Fig. 2. Plot of ln $g(\alpha)$ vs. $1/T$ for the evolved gas analysis of nickel nitrate hexahydrate.

exception of $[-\ln(1-\alpha)]$. Although in the third region $[-\ln(1-\alpha)]^n$ was selected, $n = 1$ was chosen since all other values gave values of $A < 1$.

Table 2 shows the kinetic parameters calculated from the TG data for the main decomposition. Again, the comparison of the standard deviations indicated $[-\ln(1-\alpha)]^n$ as the best fit. Selection of $n$ was based on firstly the magnitude of $A$ (eliminating $n = 1$), and secondly the recalculation of the data using a differential method developed by Dollimore and Hoath [15]. On the basis of the magnitude of $A$ and the size of the correlation coefficient, this eliminated $n = 1/3$, $1/4$, $2/3$, $2/5$, leaving $n = 1/2$.

The differences between the EGA and TG results shown in Tables 1 and 2 serve to emphasise the composite nature of TG experiments. Mechanistic interpretations of TG data for multistage reactions where overlap between stages occurs is not possible. It is when faced with reactions of this type that an accurate form of EGA such as mass spectrometry is essential [16]. In addition, the increased sensitivity afforded by a mass spectrometer allows the beginning of the reaction to be more readily determined. In this case the evolved gas in the range $\alpha = 0$–$0.073$ may be due to the hydrolysis of the nitrate as discussed earlier. It is to be expected that this process is diffusion controlled, a process described by the equation

$$kt = \left[(1-\alpha)^{-1/3} - 1\right]^2$$

TABLE 1

Kinetic parameters for the evolved gas analysis of nickel nitrate decomposition

| Equation [$g(\alpha)$] | Activation energy (kJ mole$^{-1}$) | $A$ (s$^{-1}$) | $\alpha$ Range | Temperature range (K) |
|---|---|---|---|---|
| $[(1-\alpha)^{-1/3}-1]^2$ | 66.9 | 2.15 E01 | 0–0.073 | 318–476.4 |
| $[(1+\alpha)^{1/3}-1]^2$ | 160.3 | 2.50 E11 | 0.073–0.425 | 476.4–519.4 |
| $[-\ln(1-\alpha)]$ | 53.5 | 5.90 E01 | 0.425–0.993 | 519.4–605 |

TABLE 2

Kinetic parameters for the rising temperature thermogravimetry of nickel nitrate

| Equation $[g(\alpha)]$ | Activation energy (kJ mole$^{-1}$) | $A$ (s$^{-1}$) | $\alpha$ Range | Temperature range (K) |
|---|---|---|---|---|
| $[-\ln(1-\alpha)]^{1/2}$ | 110.16 | 3.77 E08 | 0.011–0.503 | 470–502.7 |
| $[(1-\alpha)^{-1/3}-1]^2$ | 67.28 | 2.35 E03 | 0.503–0.986 | 502.7–605 |

Results for the range $\alpha = 0.073$–$0.425$ obey the equation

$$kt = \left[(1+\alpha)^{1/3} - 1\right]^2$$

This equation was derived by Komatsu and Vemura [17] for a solid state reaction between two components controlled by the diffusion of one component out of a sphere through a product layer of increasing thickness. The equation could, however, describe a solid state decomposition reaction controlled by the diffusion of a gaseous product through a solid product layer of increasing thickness. The remainder of the reaction is described by the equation

$$kt = \left[-\ln(1-\alpha)\right]$$

This could indicate diffusion [11].

If the heats of reaction are calculated using published data [18] for the two reactions

$$Ni(OH)_2 \rightarrow NiO + H_2O \qquad (a)$$

$$Ni(NO_3)_2 \rightarrow NiO + 2\,NO_2 + NO \qquad (b)$$

then $\Delta H^0 = 59.2$ and 340.2 kJ mole$^{-1}$ for a and b, respectively. Although $\Delta H^0$ may not necessarily equal $E$ (the activation energy) they should be of the same magnitude. We thus suggest that peak D on the DTA trace reflects the high value of $\Delta H^0$. This explains the correspondence of peak D to the EGA trace which is of reaction (b) only. The low values of $E$ calculated from the EGA data confirm the rate determining steps as diffusion controlled.

## SUMMARY

The thermal decomposition of nickel nitrate hexahydrate has been studied using thermogravimetric analysis and an evolved gas analysis system based on a mass spectrometer. Differential thermal analysis and theoretical thermodynamic calculations were used to provide complementary data. The following points summarise the results obtained.

(1) The decomposition begins at a temperature of 315 K, the only product of any significance being water up to 400 K; thereafter water and NO/NO$_2$ are evolved.

(2) Hydrolysis of the nitrate by water vapour occurs at temperatures prior to the main decomposition.

(3) The rate controlling steps, considering both kinetic and theoretical thermodynamic data, are diffusion controlled for the main nitrate decomposition.

(4) Evolution of $NO/NO_2$ was found to occur in two main stages, the first having Arrhenius kinetic parameters of $E = 160.3$ kJ mole$^{-1}$, $A = 2.50 \times 10^{11}$ s$^{-1}$, and the second $E = 53.5$ kJ mole$^{-1}$, $A = 5.90 \times 10^{1}$ s$^{-1}$.

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