

## Kinetic analysis of the dehydration and linkage isomerization of potassium hexanitronickelate(II) hydrate

J.E. House, Jr. \*, Julie K. Muehling and Christopher C. Williams

*Department of Chemistry, Illinois State University, Normal, IL 61761 (USA)*

(Received 18 November 1992)

### Abstract

The dehydration of  $K_4 [Ni(NO_2)_6] \cdot xH_2O$  has been studied by TG and DSC in a highly replicated study. Mass loss data indicate that the material used in this work contained 2.685% water, and this is consistent with the compound being formulated as  $K_4 [Ni(NO_2)_6] \cdot 0.75H_2O$ . Out of 128 combinations of the  $\alpha, T$  data sets from TG experiments, the Reich and Stivala procedure gave the best fit with the A2 rate law 55 times and with the A1.5 rate law 41 times. Out of 48 combinations of  $\alpha, T$  data sets obtained from DSC experiments, the A2 rate law fitted best in 29 cases and the A1.5 in 8 cases. In contrast to previous studies, there is no evidence that the reaction follows a first-order process but rather the dehydration appears to be best considered as following an Avrami rate law with an index of 1.5–2.

### INTRODUCTION

With increasingly sophisticated instrumentation and data analysis techniques has come a greater reliance on non-isothermal methods for studying the kinetics of solid state reactions. However, such studies have shown the necessity for considering sample-to-sample variations [1, 2]. Kinetic studies have been carried out on reactions involving the dehydration of many materials. For example, the dehydrations of  $CaC_2O_4 \cdot H_2O$  [3] and  $K_2 [Cu(C_2O_4)_2] \cdot 2H_2O$  [4] are frequently used in testing kinetic methods. While most hydrated compounds can be dehydrated without inducing other changes, the dehydration of  $K_4 [Ni(NO_2)_6] \cdot H_2O$  is known to involve the isomerization of two of the nitrite groups so that  $K_4 [Ni(NO_2)_4(ONO)_2]$  is produced as two of the Ni–NO<sub>2</sub> linkages are converted into Ni–ONO linkages [5]. In fact, Goodgame and Hitchman [5] showed that the hydrated compound could not be dehydrated without causing the linkage isomerization. Our initial work on this process and the subsequent decomposition of

\* Corresponding author.

the anhydrous  $K_4[Ni(NO_2)_4(ONO)_2]$  was carried out using DSC [6]. In that early study, two types of endothermic peaks were observed in the dehydration region. More often, a peak was observed which corresponded to dehydration (mass loss 3.5%) and linkage isomerization. In a few experiments, however, an endothermic peak of different shape was observed which was accompanied by a small (0.76%) mass loss, and it appeared to be associated primarily with the linkage isomerization and only about 20% dehydration. In a later study, TG was used to study the mass loss accompanying dehydration and DSC was used to study the dehydration and linkage isomerization [7]. Kinetic analysis was carried out using the Coats and Redfern procedure [8]. Although these early studies provided some insight as to the kinetics of the dehydration, instrumentation and data analysis techniques available at the time did not permit the type of kinetic analysis that is possible now. Accordingly, we have reinvestigated this interesting reaction using more modern approaches.

## EXPERIMENTAL

The preparation of  $K_4[Ni(NO_2)_6] \cdot H_2O$  followed essentially the method of Goodgame and Hitchman [5]. A concentrated aqueous solution of  $Ni(NO_3)_2 \cdot 6H_2O$  was added to a saturated solution of  $KNO_2$ . The latter solution was in excess. The solid compound was separated by filtration and the product was dried for several days in a desiccator.

TG studies were carried out using a Perkin-Elmer TGA-7 thermogravimetric analyzer controlled by a TAC-7 controller linked to an IBM PS/2 50Z computer. Heating rates of 2.5, 5.0, and  $10.0^\circ C \text{ min}^{-1}$  were used. DSC studies were performed using a Perkin-Elmer DSC-7 differential scanning calorimeter, also controlled by a TAC-7 controller. In the DSC studies, heating rates of 1.0, 2.0, 4.0, 5.0, and  $10.0^\circ C \text{ min}^{-1}$  were employed. The procedures employed were similar to those previously described in [4].

The fraction of the reaction completed  $\alpha$  was determined from the TG curves by comparing the observed mass loss to that corresponding to a complete reaction. In the DSC work,  $\alpha$  was determined by comparing the partial peak area up to the desired temperature to that corresponding to a complete reaction. Kinetic analysis was performed on these  $\alpha$ ,  $T$  data by the method of Reich and Stivala [9]. The rate laws tested in this method are shown in Table 1.

## RESULTS AND DISCUSSION

The dehydration of a large number of samples of the hydrated  $K_4[Ni(NO_2)_6]$  gave an average mass loss of 2.685% compared to 3.54% expected for a monohydrate. Therefore, it appears that the material prepared for this study is approximately  $K_4[Ni(NO_2)_6] \cdot 0.75H_2O$ . The

TABLE 1

Rate laws tested

A4	$[-\ln(1 - \alpha)]^{1/4}$	A3	$[-\ln(1 - \alpha)]^{1/3}$
P3	$\alpha^{1/2}$	A2	$[-\ln(1 - \alpha)]^{1/2}$
A1.5	$[-\ln(1 - \alpha)]^{2/3}$	R2	$1 - (1 - \alpha)^{1/2}$
R3	$1 - (1 - \alpha)^{1/3}$	F1	$-\ln(1 - \alpha)$
D1	$\alpha^2$	D2	$\alpha + (1 - \alpha) \ln(1 - \alpha)$
D4	$1 - (2\alpha/3) - (1 - \alpha)^{2/3}$	D3	$[1 - (1 - \alpha)^{1/3}]^2$

material prepared in our previous work contained 3.30% water in one case [6] and 3.9% in the other [7]. It appears that the actual H<sub>2</sub>O content depends somewhat on preparation and drying conditions. However, as will be discussed later, the infrared spectrum of the hydrated material showed that no linkage isomerization had taken place.

The dehydration of  $K_4[Ni(NO_2)_6] \cdot H_2O$  takes place in a single step without complicating features, as indicated in the TG curve displayed in Fig. 1. The original hydrated sample showed a broad IR band at 3600–3300  $cm^{-1}$  due to water. Weak absorptions at 833 and 809  $cm^{-1}$ , due to ONO bending vibrations of coordinated  $NO_2$  groups, were also present. After heating, the IR spectrum of  $K_4[Ni(NO_2)_4(ONO)_2]$  had peaks at 865, 846, 825, and 812  $cm^{-1}$  which are attributable to both  $-NO_2$  and  $-ONO$  groups. The positions of the peaks match those reported by Goodgame and Hitchman [5]. Thus, the reaction involves both dehydration and linkage isomerization.

In the TG studies, eight runs were carried out at each heating rate.

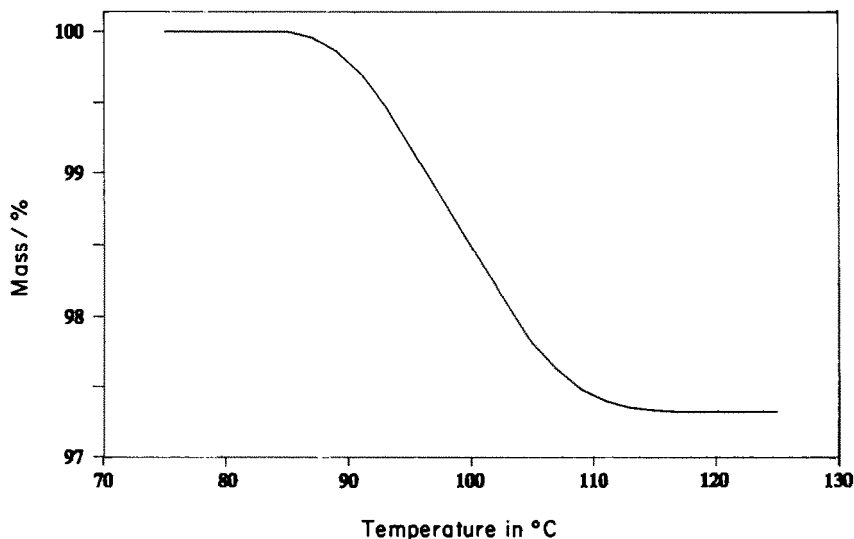


Fig. 1. A typical TG curve for the dehydration of  $K_4[Ni(NO_2)_6] \cdot 0.75H_2O$ .

Accordingly, it was possible to obtain 64 combinations of the runs at 2.5 and 5.0°C min<sup>-1</sup> and another group of 64 combinations for the 5.0 and 10.0°C min<sup>-1</sup> runs. All of these possible data combinations were analyzed by the procedure of Reich and Stivala [9]. The results of the analysis are shown in Table 2. This table shows both the best fitting and the second-best fitting rate laws: there was frequently only a small difference in the standard error of estimate (SEE) between the two mathematical expressions.

It can be seen that the results from the runs at 2.5 and 5.0°C min<sup>-1</sup> gave

TABLE 2

Results of the kinetic analysis of the TG and DSC data

Method	Heating rates <sup>a</sup>	Rate law	Indicated best fit <sup>b</sup>	Indicated second-best fit <sup>b</sup>
TG	5 and 10 <sup>c</sup>	A2	24	18
		A1.5	19	7
		P3	11	25
		A3	6	0
		R2	4	10
		R3	0	4
TG	2.5 and 5 <sup>c</sup>	A2	31	9
		A1.5	22	16
		R2	6	9
		R3	1	10
		P3	1	16
		F1	3	1
DSC	5 and 10 <sup>d</sup>	A3	0	3
		A1.5	6	2
		A2	3	4
		A3	3	0
		F1	2	0
		P3	1	3
		R3	1	0
		A4	0	1
DSC	2 and 4 <sup>d</sup>	D1	0	2
		R2	0	4
		A2	14	1
		A1.5	2	10
		A3	0	2
		R2	0	1
DSC	1 and 2 <sup>d</sup>	P3	0	2
		A2	12	0
		A3	4	0
		P3	0	16

<sup>a</sup> Heating rate in °C min<sup>-1</sup>. <sup>b</sup> Number of times this rate law provided the best fit or the second-best fit to the  $\alpha, T$  data. <sup>c</sup> There were 64 run combinations tested. <sup>d</sup> There were 16 run combinations tested.

the best fit with an A2 rate law (31 of 64 cases). The A1.5 rate law gave the best fit for 22 of the 64 cases. Thus, 53 of the 64 run combinations gave a best fit with the A1.5 or A2 rate laws. The A2 and A1.5 rate laws gave second-best fits to the data in 9 and 16 cases, respectively.

When the data for TG runs at 5.0 and 10.0°C min<sup>-1</sup> were analyzed, the A2 rate law was indicated as the best fitting one in 24 cases and the A1.5 provided the best fit in 19 cases. Thus, 43 of the 64 data combinations indicated an Avrami A2 or A1.5 rate law, and another six combinations gave the best fit with an A3 rate law. Also, 25 combinations yielded the second-best fit with these rate laws. Consequently, it is quite clear that the preponderance of the data from the TG studies indicate that the dehydration of K<sub>4</sub>[Ni(NO<sub>2</sub>)<sub>6</sub>] · 0.75H<sub>2</sub>O follows an Avrami rate law with an index of 1.5–2, with the A2 rate law giving the best fit for more of the combinations. The consistency of the results indicates that there is not a significant difference when heating rates of 2.5 and 5.0°C min<sup>-1</sup> are used or when heating rates of 5.0 and 10.0°C are used.

Analysis of the TG data in our earlier kinetic study [7] was carried out according to the Coats and Redfern procedure [8]. The dehydration process was interpreted in terms of a first-order rate law. DSC curves were analyzed by the procedure of Thomas and Clarke [10], with a two-step process being indicated. A recent study of the dehydration of K<sub>2</sub>[Cu(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>] · 2H<sub>2</sub>O has shown that these data analysis procedures are inadequate and can lead to totally erroneous results [4] when the reacton follows a rate law that cannot be represented as

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n$$

Although a good fit to this equation may be achieved with *some* value of *n*, it may still be the incorrect rate law.

Figure 2 shows a typical DSC curve for the dehydration of K<sub>4</sub>[Ni(NO<sub>2</sub>)<sub>6</sub>] · 0.75H<sub>2</sub>O. The DSC curves were analyzed by determining partial areas to obtain  $\alpha, T$  data in the range 95–118°C. Table 2 also shows the results of analyzing the  $\alpha, T$  data from the DSC studies by the Rich and Stivala procedure. It can be seen that when combinations of the runs at 1.0 and 2.0°C min<sup>-1</sup> are analyzed, the A2 rate law gave the best fit to the data in 12 of the 16 combinations. It is interesting that in each of the 16 combinations of data sets, the second-best fitting rate law was P3. An A2 rate law was indicated in 14 of the 16 combinations of data sets for runs at 2.0 and 4.0°C min<sup>-1</sup>, with A1.5 providing the best for the remaining two combinations. For the 16 combinations of data from runs at 5.0 and 10.0°C min<sup>-1</sup>, six gave the best fit with the A1.5 rate law and three gave the best fit with the A2 rate law. When the 48 combinations of data sets from DSC runs are considered collectively, 29 cases gave the best fit with the A2 rate law and 8 gave the best fit with the A1.5 expression.

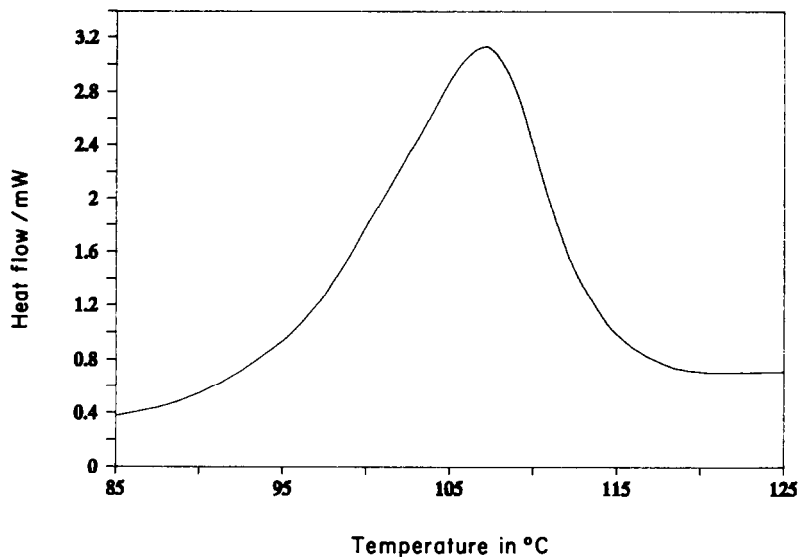


Fig. 2. A typical DSC curve for the dehydration and linkage isomerization in  $K_4[Ni(NO_2)_6] \cdot 0.75H_2O$ .

Due to small sample-to-sample variations in the  $\alpha, T$  data, no kinetic analysis technique can be relied upon to indicate a unique rate law when several sets of data are considered [1, 2]. An examination of the distribution of the indicated rate laws obtained from numerous experiments can be made in order to indicate the consistency of the results. Figure 3 shows such a distribution diagram for the 176 data combinations analyzed in this work.

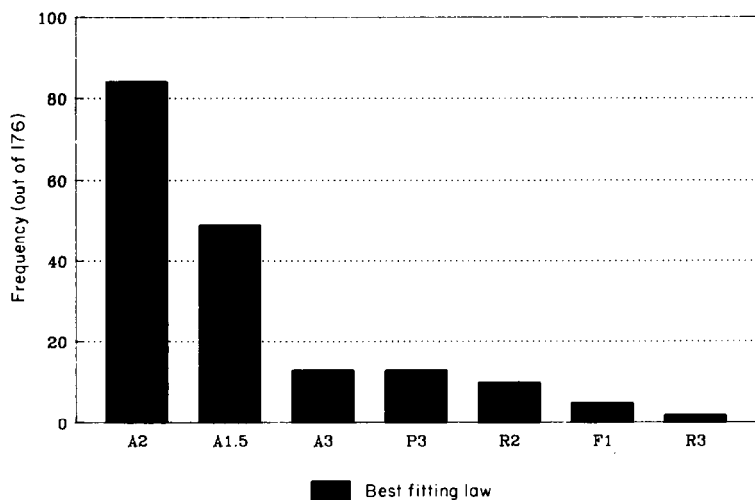


Fig. 3. A distribution diagram showing the rate laws indicated for 176 combinations of TG and DSC runs analyzed by the procedure of Reich and Stivala [9].

Clearly, the Avrami rate laws A2 and A1.5 represent the bulk of the kinetic data. There is no indication that the first-order process previously reported [6, 7] from treating the TG data by a Coats and Redfern method realistically represents this reaction. TG and DSC techniques appear to be equally valid for investigating the reaction studied in this work. Because TG reflects mass loss which accompanies dehydration and DSC reflects heat flow which might accompany both dehydration and linkage isomerization, it is interesting that the two techniques agree so well with regard to the rate law indicated. This may indicate that the two processes are completely simultaneous and that they are inextricably linked. Certainly no evidence was obtained in this work to indicate that the dehydration is separate from the linkage isomerization.

It is possible to perform data analysis iteratively using the expression  $[-\ln(1 - \alpha)]^{1/n}$  where  $n$  is allowed to take on any value [3]. We have chosen to retain the  $n$  values corresponding to the various nucleation models [11] although some value of  $n$  between 1.5 and 2 may have provided a slightly better fit to more of the data sets. To determine a value for  $n$  using iterative techniques in this way does not remove the effects of sample-to-sample variation [1–4] or provide more mechanistic information. In fact, the actual value of  $n$  determined in this way is still dependent on which data combinations are selected for analysis. At the present time, it is still necessary to perform highly replicated studies in order to identify a rate law with some degree of certainty.

## REFERENCES

- 1 J.E. House, Jr., *Thermochim. Acta*, 40 (1980) 225.
- 2 J.E. House, Jr., *Thermochim. Acta*, 47 (1981) 71.
- 3 H. Tanaka, S. Ohshima, S. Ichiba and H. Negita, *Thermochim. Acta*, 48 (1981) 137, and references cited therein.
- 4 J.E. House, Jr. and L.A. Marquardt, *J. Solid State Chem.*, 89 (1990) 155.
- 5 D.M.L. Goodgame and M.A. Hitchman, *Inorg. Chem.*, 6 (1967) 814.
- 6 J.E. House, Jr. and R.K. Bunting, *Thermochim. Acta*, 11 (1975) 357.
- 7 J.E. House, Jr., *Thermochim. Acta*, 32 (1979) 139.
- 8 A.W. Coats and J.P. Redfern, *Nature*, 201 (1964) 68.
- 9 L. Reich and S.S. Stivala, *Thermochim. Acta*, 62 (1983) 129.
- 10 J.M. Thomas and T.A. Clarke, *J. Chem. Soc. A*, (1968) 457.
- 11 D.A. Young, *Decomposition of Solids*, Pergamon Press, Oxford, 1966.