Journal of Thermal Analysis and Calorimetry, Vol. 96 (2009) 2, 439–441

THERMOGRAVIMETRIC STUDY OF THE DEHYDRATION REACTION OF $LiCl{\cdot}H_2O$

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The dehydration of $LiCl{\cdot}H_2O$ was studied under inert helium atmosphere by DTA/TG for different heating rates. The dehydration of $LiCl{\cdot}H_2O$ proceeds through a two step reaction between 99–110 and 160–186°C, respectively. It leads to the formation of $LiCl{\cdot}0.5H_2O$ as intermediate compound. The proposed mechanism is:

$$LiCl{\cdot}H_2O \xrightarrow{T_{d,1}} LiCl{\cdot}0.5H_2O + 0.5H_2O \quad \text{(step 1)}$$

and

$$LiCl{\cdot}0.5H_2O \xrightarrow{T_{d,2}} LiCl + 0.5H_2O \quad \text{(step 2)}$$

Based on the temperature peak of the DTA signals the activation energies of the two reactions were determined to be 240 kJ mol^{-1} (step 1) and 137 kJ mol^{-1} (step 2), respectively.

Keywords: *activation energy, chloride, dehydration, kinetics, salt*

Introduction

Numerous salts are used or envisioned for use in high temperature industrial processes or applications. Most of the time high purity salts are required to reach the requested performances or to avoid parasitic reactions which would affect the reaction efficiency. Usually, handling the salts under air is prohibited due to humidity which may be adsorbed at the salt surface and may form hydrates. Also, uncontrolled temperature drying leads to the formation of hydroxides or oxides when salts are used at high temperature.

In the case of thermal batteries lithium-based salts are used in electrolytes due to their relative low melting points compared to sodium or potassium salts. In addition, they present high ionic conductivity, which is one of the most important features for electrolytes in high temperature batteries [1]. However they are very sensitive to water vapour, and form hydrates according to Eq. (1).

$$LiX{\cdot}nH_2O \xrightarrow{T_d} LiX(n-m)H_2O + mH_2O \quad (X = Cl, Br, I) \tag{1}$$

The thermal decomposition of lithium salt hydrates LiX (*X*=Cl, Br, I) has been investigated. But for the $LiCl{\cdot}H_2O$ hydrate some discrepancies appear between the literature data ($LiCl{\cdot}H_2O$ 110 [2], 100.5 [3], 99 [4] 88°C [5], and $LiCl{\cdot}0.5H_2O$: 162 [1], 152°C [2]. The differences observed in the literature data for the decomposition temperature of these hydrates may be due to the experimental conditions as it depends on the water vapour pressure. A re-evaluation of the thermal stability of the $LiCl{\cdot}H_2O$ hydrate under inert atmosphere has been undertaken.

Experimental

Chemicals

$LiCl{\cdot}H_2O$ hydrate was purchased from Sigma-Aldrich (+99% purity). It was stored in a glove box. The hydrate was finely ground in a mortar to minimize the crystal size effect during thermal analysis.

Coupled differential thermal analysis (DTA)/ thermogravimetry (TG)

Thermal analyses were performed using a Setaram 24 thermal analyser equipped with a double oven (in order to increase the TG sensitivity and stability). Experiments were carried out under dynamic atmosphere (flow rate of 1.25 cm^3 h^{-1}) of dry helium (less than 1 ppm H_2O) with 100 mg samples. Inert alumina Al_2O_3 crucibles (100 μL) were used.

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1388–6150/$20.00

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Results and discussion

DTA/TG measurements

Thermogravimetric measurements were carried out at heating rates between 1 to 10°C min^{-1} under inert atmosphere. The temperatures of the events were derived from the peaks of the DTA curve. The values $T_{d,i}$ (i=1, 2 for the first and second dehydration steps, respectively) are reported in Table 1 and Fig1. The mass variation corresponds to the mass of crystallised water molecules lost during the heating phase divided by the mass of the hydrate $LiCl\cdot H_2O$. For each heating rate, the mass variation *vs*. temperature exhibits two well separated parts. The first part corresponds to the partial dehydration of $LiCl\cdot H_2O$ according to Eq. (2).

$$LiCl\cdot H_2O \xrightarrow{T_{d,1}} LiCl\cdot 0.5H_2O + 0.5H_2O \qquad (2)$$

According to Eq. (2) the mass variation should be equal to 12.5 mass%. The measured mass variation for the first step was close to 13.5 mass% which is in agreement with the proposed mechanism. The difference may be ascribed to an initial molar ratio $H_2O/LiCl$ slightly higher than 1. The second part of the curve was attributed to the formation of LiCl by losing half of a crystallised water molecule per $LiCl\cdot 0.5H_2O$ unit according to Eq. (3).

$$LiCl\cdot 0.5H_2O \xrightarrow{T_{d,2}} LiCl + 0.5H_2O \qquad (3)$$

Experimentally the mass loss measured during the second part of the curve was close to 13.5 mass% whereas 12.5 mass% was expected. The mass losses during the first and the second parts are equal and these results support the proposed mechanism of dehydration of $LiCl\cdot H_2O$ Eqs (2) and (3). For each mass variation observed a corresponding thermal event was recorded, allowing definition of the temperature where the dehydration reaction takes place. The first and second dehydration steps occur between 99–110 and 160–186°C, respectively. The temperature $T_{d,i}$ are shifted towards higher temperature as the heating rate is increased. Between 190 and 500°C no mass variation was recorded. Above 500°C linear mass loss was observed. It was ascribed to the progressive vaporization of the salt LiCl near its melting point under reduced pressure. At 610°C only an endothermic DTA signal was recorded without TG signal. This corresponds to the solid–liquid transformation of the LiCl salt. The melting point of LiCl was found to be close to 610°C which agrees with previous determinations made by differential scanning calorimetry with anhydrous LiCl [6]. It means that the dehydration of $LiCl\cdot H_2O$ proceeded without the hydrolysis of the salt LiCl at intermediate temperature, as it was evidenced with the LiCl–KCl eutectic at 250°C in the presence of moisture [7]. Otherwise the melting point measured would have been modified by the formation of hydroxide. In this case the melting would have corresponded to the liquidus temperature of a mixture $x LiOH\cdot(1-x)LiCl$.

Table 1 Decomposition temperature $T_{d,i\ (i=1,2)}$ of the $LiCl\cdot H_2O$ hydrates *vs*. the heating rate

β/°C min^{-1}	$T_{d,1}$/°C	$T_{d,2}$/°C
1	99	160
2	102	166
5	106	177
10	110	186

Kinetics

In the past kinetic features have been derived from thermogravimetric measurements according to the theoretical treatment proposed by Kissinger [8, 9]. The treatment uses either DTA or DTG temperature peak. The theoretical background is described below. Assuming that transformation rate can be expressed by the following expression (Eq. (4)) like most of the reactions of the type solid→solid+gas [10].

$$\frac{d\alpha}{dt} = k(T)(1-\alpha)^n \qquad (4)$$

where α is the transformation ratio, $k(T)$ the kinetic constant, T the temperature in Kelvin and n the reaction order. When the reaction rate reaches its maximum, its derivative with respect to time is equal to zero. Assuming that $k(T)$ follows an Arrhenius rate constant ($k(T)=k^0\exp(-E_a/RT)$ where E_a represents the activation energy, R is the gas constant 8.3245 J K^{-1} mol^{-1} and k^0 the pre-exponential factor), the maximum value of $d\alpha/dt$ occurs at temperature $T_{d,i}$ (DTA peak maximum temperature) defined by Eq. (5), it comes

$$\frac{d^2\alpha}{dt^2} = \frac{k^0 E_a}{RT}\exp\left(\frac{-E_a}{RT}\right)(1-\alpha)^n \beta - nk^0 \exp\left(\frac{-E_a}{RT}\right)(1-\alpha)^{n-1}\frac{d\alpha}{dt} \qquad (5)$$

The reaction rate is thus maximum when its second derivative with respect to time is zero which leads to Eq. (6):

$$\frac{E_a}{RT}(1-\alpha)^n_{max}\frac{dT}{dt} = n(1-\alpha)^{n-1}_{max}\frac{d\alpha}{dt} \qquad (6)$$

Remembering that $dT/dt=\beta$, which simplifies to Eq. (7):

$$\ln\left(\frac{\beta}{T^2}\right) = \frac{-E_a}{RT} + \ln\left(k^0\frac{R}{E_a}\right) + \ln[n(1-\alpha)^{n-1}_{max}] \qquad (7)$$

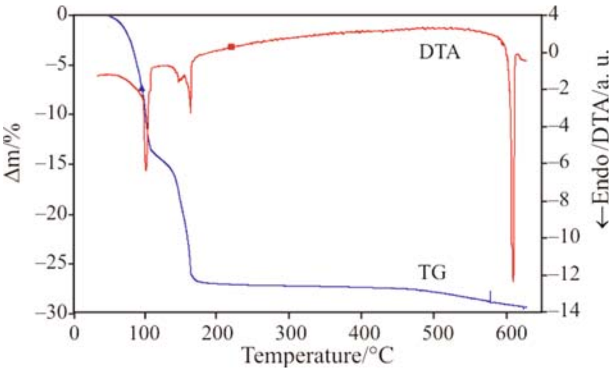

Fig. 1 TG and DTA traces recorded with a $LiCl\cdot H_2O$ sample heated at 1°C min^{-1} under He atmosphere

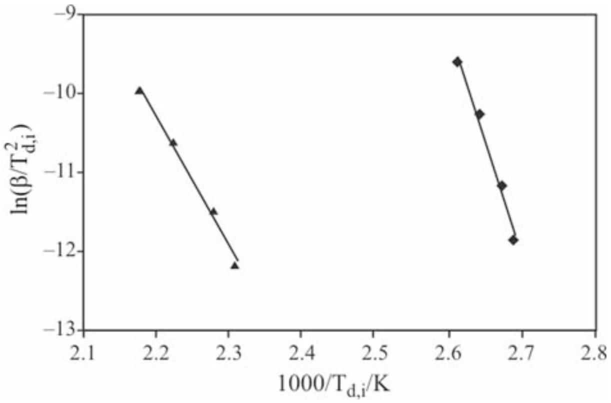

Fig. 2 Curves $\ln(\beta/T_{d,i})$ *vs*. $1000/T_{d,I}$ (K), ◆ – i=1 and ▲ – i=2 for the first and second dehydration steps, respectively

Kissinger [8] showed that the product $n(1-\alpha)^{n-1}_{\max}$ was nearly equal to unity. As indicated by equation Eq. (8) makes possible the determination of the activation energy E_a for a simple decomposition reaction regardless of the reaction order, from differential thermal analysis patterns at different heating rates. It results:

$$\ln\left(\frac{\beta}{T^2}\right)=\frac{-E_a}{RT}+\ln\left(k^0\frac{R}{E_a}\right) \tag{8}$$

Plotting $\ln(\beta/T^2_{d,i})$ *vs*. $1/T_{d,i}$ (Fig. 2) as indicated by equation Eq. 7, should give a straight line and the slope should be equal to $-E_a/R$. However, it should be pointed out that it is assumed for the calculations that activation energy is independent of the temperature. The activation energy for the dehydration steps 1 and 2 were found close to 240 and 137 kJ mol^{-1}, respectively. These values are in agreement with data cited in the literature survey of Galwey [10] for the activation energies of the reaction of dehydration of some metal chlorides.

Conclusions

The results of this work are:

- The dehydration of $LiCl\cdot H_2O$ proceeds through two steps between 99–110 and 160–186°C, respectively.
- $LiCl\cdot 0.5H_2O$ forms as intermediate compound during the first step of the reaction of dehydration of $LiCl\cdot H_2O$.
- The dehydration of $LiCl\cdot 0.5H_2O$ leads to the formation of pure LiCl.
- The activation energies of the steps 1 and 2 of the dehydration reaction of $LiCl\cdot H_2O$ are equal to 240 and 137 kJ mol^{-1}, respectively.

Acknowledgements

The results reported in this text were obtained during the thesis of the author, who acknowledges the financial support of CEA Le Ripault, LEPMI/INP Grenoble and ASB-Aerospatiale Batteries. The author thanks Jean-Claude Poignet (LEPMI/INP Grenoble), Jean-Yves Poinso (CEA Le Ripault) and Serge Schoeffert (ASB-Aerospatiale Batteries) for their continuous support during this project.

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Received: July 10, 2008
Accepted: October 2, 2008
Online First: January 12, 2009

DOI: 10.1007/s10973-008-9399-y