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Unexpected effect of pressure on the dehydration kinetics of uranyl nitrate trihydrate: an example of a Smith–Topley effect[1]

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Abstract

The dehydration of uranyl nitrate trihydrate is investigated by Controlled transformation Rate Thermal Analysis (CRTA) allowing both the control of the rate and residual pressure. The "abnormal" influence of the residual pressure above the sample, known as the Smith–Topley effect, is highlighted in a lower than usual pressure region, between 10^{-1} mbar and 5×10^{-3} mbar. Two mechanisms are distinguished: in the upper pressure region a mechanism of instantaneous nucleation and 2-dimensional nuclei growth occurs; lowering the pressure favours a 2-dimensional interfacial advancement mechanism. This type of Smith–Topley effect and its interpretation have not been previously proposed.

Keywords: Dehydration; Uranyl nitrate trihydrate; CRTA; Kinetics; Nucleation; Interfacial mechanism; Smith–Topley effect

1. Introduction

In this study, we highlight the influence of the residual pressure on the dehydration kinetics of uranyl nitrate trihydrate giving uranyl nitrate dihydrate.

This investigation forms part of a larger study that has been carried out on the industrial procedure to obtain uranium trioxide (UO_3) using dry methods via the thermolysis of uranyl nitrate hexahydrate $UO_2(NO_3)_2.6H_2O$ [1]. This thermolysis is a complex process leading to various intermediate products which can be isolated according to the experimental conditions, namely, uranyl nitrate trihydrate, dihydrate,

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[1] Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

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monohydrate and finally the anhydrous uranyl nitrate [2–7]. In a previous study, we have shown that the dehydration is only complete before the denitration commences if the residual pressure above the sample is below 20 mbar. Furthermore, two crystalline phases of anhydrous nitrate have been identified whose relative proportions vary with the residual pressure [8].

It is known that the kinetics of the dehydration of the crystallised salts do not depend in a simple manner on the water vapour pressure. This complexity is illustrated in certain cases where the rate of dehydration does not decrease continuously (for given T and α), whilst the water vapour pressure increases but passes through a maximum before decreasing again. This anomaly in the rate–pressure $r(p)$ curve was shown for the first time by Smith and Topley in the case of the dehydration of manganese oxalate dihydrate [9]. Since this first observation, this "Smith–Topley" effect has been noted for other hydrates, such as lithium sulphate monohydrate [10,11], manganese sulphate tetrahydrate and copper sulphate tri- and pentahydrate [12]. Various explanations have been given for the experimental observations, such as, for example, a lack of synchronism between the elimination of the water and the structural modification of the initial phase [10], or a recrystallisation of the dehydrated phase inducing a larger porosity which favours water elimination, or, furthermore, the existence of two types of nuclei of different shape which grow at different rates [13]. However the existence of such an effect on so many dehydrations, which can lead to either amorphous or well-crystallised products and for which it has been checked that within both the temperature and pressure regions investigated the kinetic regime is conserved, has led certain authors to generalise this phenomenon. Indeed, the hypothesis of a catalysis of the desorption by the gaseous phase [11] or the hypothesis of a coupling between the evaporation kinetics and heat transfer [14] has allowed a reproduction of the $r(p)$ curves, showing a maximum close to that observed on the experimental plots. A better accord is observed in the case of this latter hypothesis which also reproduces the minimum of the $r(p)$ curve. Furthermore, this particularity of the $r(p)$ curve, equally observed in the case of the simple evaporation of water in a similar range of pressure (10^{-1}–5 mbar), lends credibility to this latter hypothesis of a coupling between the evaporation kinetics and heat transfer [14].

In this study, an attempt will be made, using a different hypothesis to those cited previously, to reconstitute a Smith–Topley effect.

2. Experimental

2.1. Sample and methodology

The uranyl nitrate trihydrate was obtained by the thermolysis of uranyl nitrate hexahydrate (Normapur quality, Prolabo) by controlling the pressure above the sample at a constant value of 10^{-2} mbar. This was made possible with the aid of Controlled transformation Rate Thermal Analysis (CRTA). In this method, the furnace heating is controlled by a quantity directly related to the reaction advancement in such a way that its value follows a predetermined programme [15].

2.2. *Apparatus*

In one of the simplest set-ups following this principle [16], the thermolysis is carried out "under vacuum": it is the signal produced by a Pirani gauge which measures the total residual pressure of the gases produced by the thermolysis, which is kept constant, controlling the furnace heating via a proportional, integral and differential (PID) regulation. With this apparatus it is possible to work under a controlled residual pressure in the region from 10^{-3} to 100 mbar and in the temperature region between -30 and 100°C. The coupling of this apparatus with a mass spectrometer allows one to constantly follow the nature of the gaseous phase produced by the thermolysis. As long as the gaseous phase produced has the same composition, controlling the signal produced by the Pirani gauge at a steady value means that the gas pressure is kept constant, as is the gas flow evacuated through a constriction to the pumping system (in fact, this gas flow depends on the geometry of the constriction and the pressure difference on either side of it). As soon as a stationary state is attained, this gas flow is equal to the rate of production of the gaseous phase which is thus constant.

The use of a second constriction, placed between the Pirani gauge and the sample, permits an increase of the residual pressure above the sample without changing the value of the production rate of the gaseous phase.

With this apparatus, it is possible to select a constant reaction rate slow enough to minimise the pressure and temperature gradients within the sample which are the principal causes of irreproducibility of the thermolysis and which mask the actual chemical kinetics. Thus, we have been able to show that when the thermolysis of uranyl nitrate hexahydrate is carried out under a residual pressure of 5×10^{-2} mbar, over a sufficiently long time interval (around 100 h), it is possible to show five decomposition steps (Fig. 1) forming, successively, the trihydrate (point A), dihydrate (point B), monohydrate (point C), anhydrous nitrate (point D) and finally uranium trioxide (point E). To obtain the trihydrate, it is thus sufficient to stop the analysis after the first step at point A in Fig. 1. It has been verified by X-ray analysis that the product obtained is a pure, well-crystallised phase [8].

2.3. *Treatment of data*

From the experimental CRTA curve, it is possible to analyse kinetically each decomposition step, to evaluate the activation energy and to determine the most probable reaction mechanism. The methodology described in a previous study [17] is summarised below.

First the temperature–time experimental thermogram is converted to standard coordinates of the degree of reaction (α) against temperature. The degree of reaction is defined as 0 at the start of the reaction (for $t = t_0$) and 1 at the end of the step ($t = t_f$). The times t_0 and t_f correspond respectively to the time where the residual pressure imposed above the sample is attained and where the pressure drops (Fig. 1). Insofar as the rate of

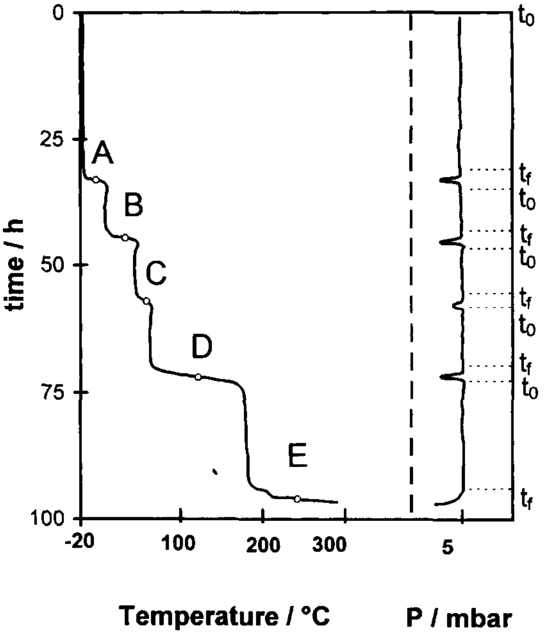


Fig. 1. Thermal decomposition of uranyl nitrate hexahydrate under a residual pressure of 5×10^{-2} mbar and at a rate of 0.01 h^{-1}. Right: pressure recording showing the fall and rise of pressure between two successive steps.

decomposition is constant, one can write

$$\int_0^{\alpha} \mathrm{d}\alpha = C \int_{t_0}^{t} \mathrm{d}t \quad \text{where } C = \frac{1}{t_f - t_0}$$

so it is possible to calculate, at every moment in time, the degree of reaction via the relationship

$$\alpha = (t - t_0)/(t_f - t_0)$$

The expression of the rate law is

$$\mathrm{d}\alpha/\mathrm{d}t = k(T)f(\alpha)$$

where $f(\alpha)$ is taken as one of the ten functions put forward by Sharp et al. [18] and which characterise a certain number of elementary reactions, such as interfacial advancement, nucleation and nuclei growth, and finally diffusion. The rate coefficient $k(T)$ follows the Arrhenius law

$$k(T) = A\exp(-E_a/RT)$$

where A is the pre-exponential factor, E_a is the Arrhenius activation energy, T is the thermodynamic temperature and R is the gas constant.

For a thermolysis which is carried out at a constant rate by CRTA, the activation energies may be determined by the rate jump method [19]. The principle of this method consists of decomposing the sample alternatively at two different rates with a ratio r_r. The consecutive thermal response to these rate jumps allows an evaluation at a given degree of reaction α, at temperatures T_1 and T_2 corresponding to each of these two rates. It is thus possible to calculate the energy of activation throughout a single step without making any assumption about the reaction mechanism

$$E_a = \frac{RT_1T_2}{T_1 - T_2}\ln(r_r)$$

For each step obtained at constant rate, Criado et al. have shown [20] that the shape of the isokinetic curves is characteristic for each mechanism. Indeed, mechanisms of instantaneous nucleation and nuclei growth give rise to curves with a minimum α_m ($\alpha_m = 0.393$ for the 2-dimensional and $\alpha_m = 0.487$ for the 3-dimensional mechanism respectively). Mechanisms limited by diffusion phenomena give rise to curves with an inflexion point (with the exception of 1-dimensional diffusion), and mechanisms governed by interfacial advancement produce curves which show neither a minimum nor an inflexion point. It is thus possible to draw theoretical curves for each mechanism using the activation energy measured via the rate jump method, the value of the imposed reaction rate and a value of the pre-exponential factor A, chosen such that the theoretical curve coincides with the greatest number of points on the experimental curve.

It is then possible to use a graphic approach which consists of comparing the experimental kinetic curve with the theoretical curves that can be obtained from the different functions of α. Our kinetic treatment of the data is much more selective than the traditional direct approach, derived from the method of Sharp and Wentworth [21]. Their method consists of plotting $\ln[\{d\alpha/dt\}/f(\alpha)]$ as a function of $1/T$ with the aim of determining the mechanism which gives the best linear regression. The approach leads to values of the activation energy which are very strongly dependent on the precision with which the degree of reaction is defined. It can be shown that an error of 1% in the determination of α can lead to an error of over 10% in the activation energies.

3. Results

3.1. Measurement of the activation energy

Fig. 2 represents the rate jumps carried out during the thermal decomposition of uranyl nitrate trihydrate which corresponds to the conversion to the dihydrate. The residual pressure imposed is 5×10^{-3} mbar. The ratio of the rates is fixed at a value of 4 and the fastest rate of decomposition does not exceed 0.02 h^{-1}. The values of the activation energy deduced from this thermogram lead to a value of 104 kJ mol^{-1} within an uncertainty of 10%.

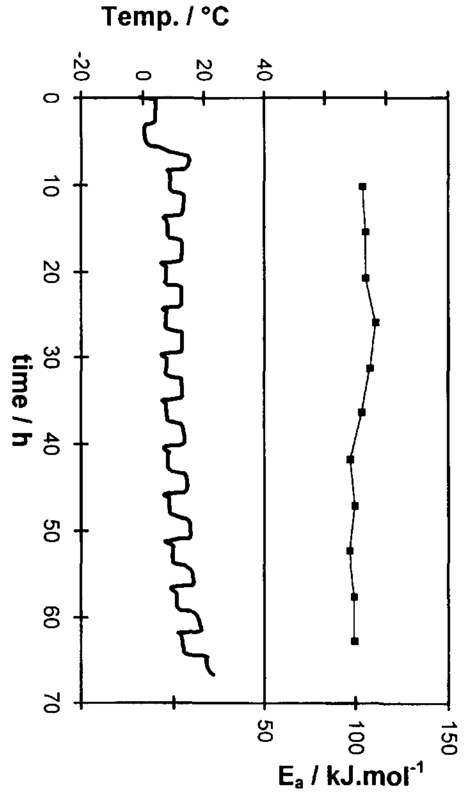


Fig. 2. Measurement of the activation energies by the rate jump method. Residual pressure = 5×10^{-3} mbar, ratio of rates $r_1/r_2 = 4$, and $r_1 < 0.02$ h^{-1}.

3.2. *Determination of the most probable reaction mechanism*

Fig. 3 represents the CRTA curve (coordinates α–T) obtained for this step under a residual pressure of 10^{-1} mbar and for a rate of 0.01 h^{-1}. This curve presents a minimum which is characteristic of a mechanism of nucleation and nuclei growth. It can be seen that an almost perfect coincidence occurs between the experimental curve and the theoretical curve obtained from a mechanism of instantaneous nucleation and 2-dimensional nuclei growth, calculated with an activation energy of 104 kJ mol^{-1}, a pre-exponential factor of 1.5×10^{13} s^{-1} and a rate of 4×10^{-6} s^{-1}.

3.3. *Influence of pressure on the reaction mechanisms of the dehydration of the uranyl nitrate trihydrate*

Under a residual pressure of 5×10^{-3} mbar, with the previous rate of decomposition, the experimental CRTA curve is not a simple one (Fig. 4). It would seem that it is the 2-dimensional interfacial advancement that most resembles part of the experimental

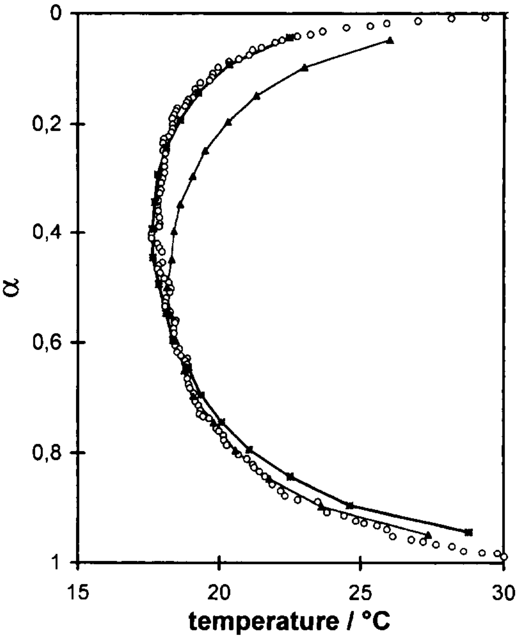


Fig. 3. Reaction mechanism of the dehydration of uranyl nitrate trihydrate under a residual pressure of 10^{-1} mbar and at a rate of 0.01 h^{-1}. ○, experimental thermogram; ■, theoretical curve characteristic of a mechanism of nucleation and 2-dimensional nuclei growth (A_2), rate $= 4 \times 10^{-6} s^{-1}$, $E = 104$ kJ mol^{-1}, $A = 1.52 \times 10^{13} s^{-1}$; ▲, theoretical curve characteristic of a mechanism of nucleation and 3-dimensional nuclei growth (A_3), rate $= 4 \times 10^{-6} s^{-1}$, $E = 104$ kJ mol^{-1}, $A = 1.13 \times 10^{13} s^{-1}$.

curve (part B). The other part of the curve (part A), taken separately, seems characteristic of a nucleation and nuclei growth type mechanism. The position of the minimum (1/3 of part A) would seem to indicate a 2-dimensional mechanism, which is consistent with the geometry of the mechanisms defined previously.

4. Discussion

These results indicate that the residual pressure influences the reaction mechanism. A theoretical study of the thermodynamics of nucleation has also shown the influence of the pressure on the nucleation process which can pass from a phenomenon of continuous nucleation to a separate nucleation–nuclei growth phenomenon [22].

In the present case of the thermal decomposition of uranyl nitrate trihydrate, we have observed that a decrease in water vapour residual pressure leads to a progressive evolution of the reaction mechanism from that of instantaneous nucleation and 2-dimensional nuclei growth towards one close to that of interfacial advancement. The first part A of the thermogram obtained at the residual pressure of 5×10^{-3} mbar could be interpreted as a nucleation of the reaction within a zone close to the surface as

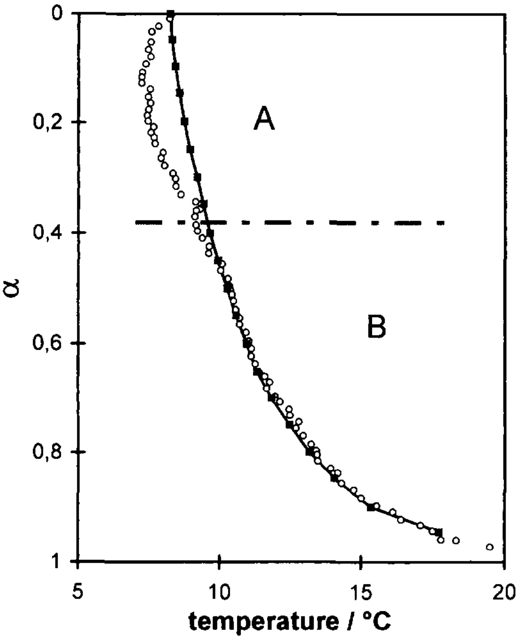


Fig. 4. Reaction mechanism of the dehydration of uranyl nitrate trihydrate under a residual pressure of 5×10^{-3} mbar and at a rate of $0.01\ h^{-1}$: ○, experimental thermogram; ■, theoretical curve characteristic of a mechanism of 2-dimensional interfacial advancement (R_2), rate $= 4 \times 10^{-6} s^{-1}$, $E = 104\ kJ\,mol^{-1}$, $A = 6.38 \times 10^{13} s^{-1}$.

schematised in Fig. 5a. The minimum of the temperature obtained in part A (Fig. 4) would thus correspond to the moment where the nuclei overlap (Fig. 5b). Finally, the change in CRTA curve behaviour (part B in Fig. 4) visible from $\alpha = 0.33$, may correspond to an overlap of the nuclei such that a mechanism of two-dimensional interfacial advancement occurs (Fig. 5c).

In a separate study we have observed that in the case of the thermal decomposition of lithium sulphate monohydrate carried out by CRTA, a decrease in water vapour residual pressure from 10^{-3} to 10^{-5} mbar changes the nucleation and nuclei growth mechanisms into one of interfacial advancement [23].

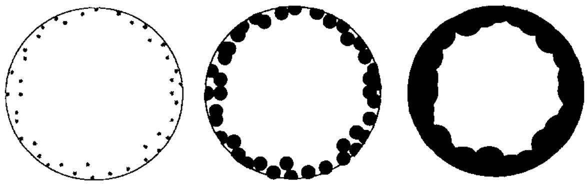
In view of these results, it is interesting to construct a plot of the rate against residual pressure for a given temperature and degree of reaction, taking into account the variation of the reaction mechanism with the pressure observed experimentally.

Therefore, for the following pressure intervals:

(i) $p \leq p_1$: the reaction is uniquely governed by a 2-dimensional interfacial advancement mechanism;

(ii) $p_1 < p < p_2$: a mixed regime occurs with an increase in the proportion of that governed by nucleation and nuclei growth for increasing residual pressures;

(iii) $p \geq p_2$: the reaction is uniquely governed by a nucleation and 2-dimensional nuclei growth mechanism.



(a) (b) (c)

Fig. 5. Schematic diagram of a mechanism of surface nucleation (a) with nuclei growth (b), leading to a mechanism of interfacial advancement (c).

When there is only an instantaneous nucleation followed by a 2-dimensional nuclei growth mechanism, the reaction rate is equal to

$$d\alpha_N/dt = kf_N(\alpha_N) = k2(1-\alpha_N)[-\ln(1-\alpha_N)]^{1/2} \quad (1)$$

and when there is only a 2-dimensional interfacial advancement, the rate is

$$d\alpha_A/dt = k'f_A(\alpha_A) = k'(1-\alpha_A)^{1/2} \quad (2)$$

Here the indices "N" and "A" relate to the mechanisms of nucleation and interfacial advancement respectively.

Suppose $k = k'$ for the same temperature. In the two pressure intervals where the reaction mechanism is unique, the rate is defined by relations (1) and (2) above.

In the intermediate pressure interval, one defines the rate by the relation

$$d\alpha/dt = k\,[f_A(x_A\,\alpha) + f_N(x_N\,\alpha)]$$

with $x_A = (\alpha_A/\alpha)$, $x_N = (\alpha_N/\alpha)$ and $\alpha = (\alpha_A + \alpha_N) = \text{constant}$.

On taking into account these hypotheses, we may construct the rate (r) against pressure (p) curve for $\alpha = 0.4$. We see a maximum (Fig. 6) comparable with that observed by Smith and Topley.

5. Conclusion

This study highlights the influence of residual pressure on the reaction mechanism of the dehydration of uranyl nitrate trihydrate to dihydrate in the range of residual pressure between 10^{-1} and 5×10^{-3} mbar. We observe a change in the shape of the thermograms obtained by Controlled transformation Rate Thermal Analysis. Under a water vapour residual pressure of 10^{-1} mbar, we have shown that the theoretical curve of a mechanism of instantaneous nucleation and 2-dimensional nuclei growth constructed on taking into account the activation energy measured by the rate jump method, is perfectly coincident with the experimental curve. A decrease in the residual pressure to 5×10^{-3} mbar favours nucleation and nuclei growth on the surface of the

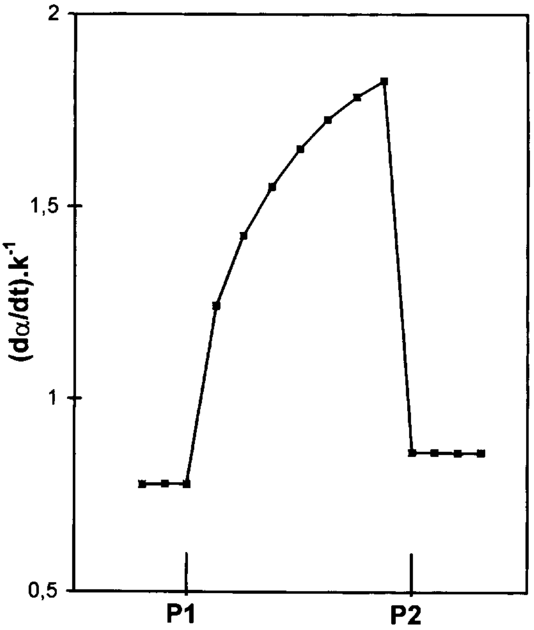


Fig. 6. Consequence of a change in reaction mechanism with the residual pressure on the plot of rate against pressure for $\alpha = 0.4$ (passage from a 2-dimensional interfacial advancement mechanism to one of nucleation and 2-dimensional nuclei growth with the increase in pressure).

sample, which ultimately leads to a mechanism of 2-dimensional interfacial advancement.

With these experimental results, we can construct the curve giving the variation of the reaction rate with the residual pressure, taking into account a change in the mechanism due to the variation of pressure, and give another explanation for the abnormal variation of the rate, known as the Smith–Topley effect.

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