

KINETICS OF DEHYDRATION OF URANYL FUMARATE DIHYDRATE UNDER ISOTHERMAL AND NON-ISOTHERMAL CONDITIONS.

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ABSTRACT

The kinetics of thermal dehydration of the title compound have been studied by both isothermal and non-isothermal procedures. The dehydration reaction of this compound takes place in a single step in the temperature range 110-150°C or it can be a stepwise reaction at higher temperature and depending on the experimental conditions, the monohydrated or hemihydrated uranyl fumarate are isolated as intermediates.

The isothermal procedures yield very reliable kinetic parameters and they have been calculated by different methods, but they are not in good agreement with those calculated from the dynamic runs, when the Coats and Redfern method is used in their calculations.

INTRODUCTION

The kinetics of dehydration of crystalline hydrates have been studied in some detail (1); this is not the case with the uranyl carboxylate compounds. Here we report on the determination of the kinetic parameters on crystals and powdered samples of uranyl fumarate dihydrate under several experimental conditions that cause a stepwise dehydration.

METHODS

Experimental

Uranyl fumarate dihydrate has been obtained as described elsewhere (2). The isothermal gravimetric runs were performed in air atmosphere using a 951 Dupont Thermogravimetric Analyzer joined to a 990 Dupont Thermal Analyzer, at the temperatures indicated in Table 1. About 8 mg of crystals were weighed in each run and they were placed in open pans or sealed cups. Powdered samples which passed through a 200 mesh sieve were also used. The dynamic TG traces obtained at the different heating rates (Table 2) were recorded under the same experimental conditions. Microscopic observations of single crystals of the compound were made by using a Karl Zeiss Wetzlar microscope with a hot stage attachment.

RESULTS AND DISCUSSION

Thermal Analysis

The DTA curve of this compound, when obtained in the high temperature cell together with the TG curve recorded in the open pan, show that dehydration occurs in a single step; but when the compound is heated in the DTA intermediate cell or the TG curves are recorded with the samples enclosed in sealed cups and depending on the applied pressure, the dehydration occurs in two consecutive steps; the uranyl fumarate monohydrate or hemihydrate are isolated as intermediates, the experimental weight losses calculated for the first steps correspond to the evolution of one or one and a half water molecules respectively.

When the same experiments are carried out on powdered samples, the evolution of the two water molecules takes place in a single step and no intermediates can be isolated.

Isothermal studies

The reduced time method (3) leads to the best fit for the Avrami-Erofe'ev equation $\{-\ln(1 - \alpha)\} = (kt)^n$, where $n = 2$ for dehydrations carried out in open conditions or on powdered samples and $n = 3$ when the reactions are carried out in sealed cups. The same best fits were also obtained by means of a computer program (4). The activation energies and pre-exponential factors obtained are summarized in Table 1.

The opacity observed on the {011} faces of single crystals of the compound isothermally heated on the hot stage of the microscope indicates that nucleation occurs at these faces (Fig.1.a) and the anhydrous product moves into the bulk. The kinetics of dehydration under these experimental conditions should be described by (5)

$$\alpha = L_1 L_2 - (L_1 - 2x)(L_2 - 2y) / L_1 L_2 \quad (1)$$

x and y can be calculated from simple geometry as a function of τk , where k is the rate constant for the interfacial growth and $\tau = t - t_0$, where t the actual time and t_0 the time for the establishment of the interface. The activation energy calculated from this analysis is 15,87 Kcal.mol⁻¹ and $A = 8,07 \times 10^6$ mm.min⁻¹. It can be assumed that once the nuclei have been formed on the {011} faces, they overlap and the two-dimensional growth of the interface from $\tau > 0$ could also be described by the contracting envelope model.

An analogous kinetic analysis cannot be done on crystals dehydrated in sealed cups since the interfacial growth is not regular (see Fig.1.b) and direct microscopic observations are not possible under these experimental conditions.

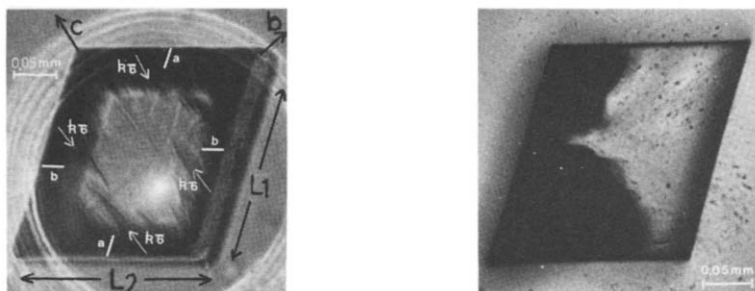


Fig.1. Micrographs of partially dehydrated single crystals of $[\text{UO}_2(\text{C}_4\text{H}_2\text{O}_4)(\text{H}_2\text{O})_2]$
(a) Open pan. (b) Sealed cups.

TABLE 1

Kinetic parameters obtained for the isothermal dehydration reaction of uranyl fumarate dihydrate under several experimental conditions.

Experimental conditions	T(°C)	Method of analysis	Ea (Kcal/mol)	A (min^{-1})	α range
CRYSTALS open pan	110,115	reduced time plot, A_2	16,45	$3,60 \times 10^8$	0,10-0,70
	120,125	geometrical	15,87	$8,07 \times 10^6 \text{ mm/min}$	
		α/t linear region	15,80	$1,70 \times 10^8$	
sealed cups - $1\frac{1}{2}\text{H}_2\text{O}$	145,150	reduced time plot, A_3	20,02	$7,14 \times 10^9$	0,16-0,70
	155,160	α/t linear region	19,41	$3,60 \times 10^5$	
sealed cups - $1\text{H}_2\text{O}$	145,155	reduced time plot, A_3	16,57	$8,55 \times 10^7$	0,25-0,80
	160,170	α/t linear region	16,38	$7,52 \times 10^7$	
POWDERED SAMPLES	100,105	reduced time plot, A_2	26,10	$1,52 \times 10^{12}$	0,17-0,70
	115,125	α/t linear region	25,50	$4,59 \times 10^{13}$	

On the other hand, the slopes of the linear regions of the α/t plots at each temperature were taken as directly proportional to the rate constant of the interfacial growth (5) and the Arrhenius plot yielded the activation energy and pre-exponential factor indicated in Table 1. The same calculations were made on the α/t plots obtained for the isothermal dehydration reactions of powdered samples or crystals enclosed in sealed cups and the results obtained are summarized in Table 1.

Non-isothermal studies

The experimental data obtained from the non-isothermal runs were analyzed by the Coats-Redfern and the Ozawa methods. In general, agreement between the activation energies calculated for the isothermal and non-isothermal dehydration reactions at high heating rates was obtained when the following equation was applied:

$$\ln g(\alpha) / T^2 = \ln \frac{AR}{E\beta} - \frac{E}{RT} \quad (2)$$

where $g(\alpha)$ is the rate equation deduced from the isothermal procedure, nevertheless the Ozawa method leads to the best agreement when it can be applied ($20 < E/RT < 60$)(6).

TABLE 2

Kinetic parameters obtained for the non-isothermal dehydration reactions of uranyl fumarate dihydrate under several experimental conditions.

Experimental conditions	(degree/min)	Method of analysis			
		Coats-Redfern		Ozawa	
		Ea(Kcal/mol)	A(min ⁻¹)	Ea(Kcal/mol)	A(min ⁻¹)
CRYSTALS open pan	2	40,07	7,89x10 ²¹		
	10	26,56	6,68x10 ¹³		
	20	16,47	2,50x10 ⁸		
sealed cups -1½H ₂ O	5	17,72	1,31x10 ⁸		
	10	14,66	5,00x10 ⁶	20,12	2,26x10 ⁹
	20	14,03	2,45x10 ⁶		
sealed cups -1H ₂ O	2	29,52	3,52x10 ¹⁴		
	10	18,30	3,50x10 ⁸		
	20	18,79	4,74x10 ⁸		
POWDERED SAMPLES	1	51,74	3,80x10 ²⁸		
	2	38,53	7,00x10 ²⁰	26,76	8,15x10 ¹³
	20	24,95	1,31x10 ¹³		

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