D22

Dehydration Kinetic for Fumarate Dioxouranium(VI) Dihydrate Single Crystals

M. L. DE PAZ

Departamento de Q. Inorgànica, Universidad Complutense, Madrid-3, Spain

and R. M. ROJAS*

Instituto de Q. Inorgànica 'Elhúyar' del C.S.I.C., Serrano, 113 bis, Madrid-6, Spain

The crystal structure and thermal behaviour at linear heating rate for uranyl fumarate dihydrate have been described elsewhere [1]. It has been shown that the experimental procedure deeply modifies the dehydration process and under very particular conditions the monohydrate or the hemihydrate are formed as independent and stable intermediates.

In order to elucidate the mechanism through which the dehydration processes occur, the kinetics of these reactions under different experimental conditions have been investigated.

The compound has been prepared as described and small batches of the crystals (about 8 mg) in open pan or sealed cups were isothermally heated. The weight changes were followed by means of a Dupont 951 Thermogravimetric Analyzer. The isothermal temperatures were selected according to the previously recorded TG curves (Table I).

The plots of the F(α) values calculated from the experimental α(fraction reacted) *vs.* $t/t_{0.5}$ fit curves that correspond with the Avrami equations (Fig. 1). The values for n were checked by means of the Hancock and Sharp '1n an method' [3] and the activation energy for the different dehydration reactions were calculated from the Arrhenius plots (Fig. 2 and Table I).

The kinetics of the dehydration of the title compound both in still air or self-generated atmospheres can be adequately described over the entire dehydration ranges by the Avrami equations A_2 or A_3 respectively. In the former situation a bidimensional growth mechanism is proposed, while in the latter one the nuclei growth three- dimensionally. Direct observations of the partially dehydrated crystals (Fig. 3) confirm these mechanisms; the formation of many opaque bands in well delimited crystallographic planes appeared when the crystals were heated in open air atmosphere while in sealed cups, both low and medium pressure, very broad opaque zones were formed throughout the bulk of the crystal.

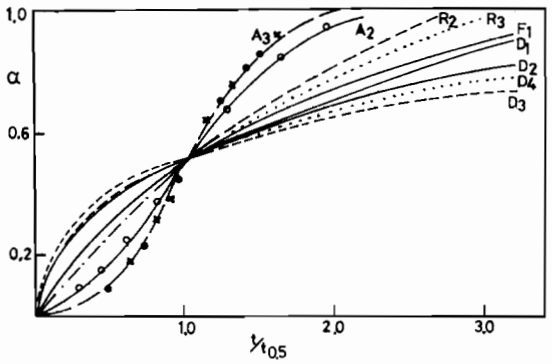


Fig. 1. Dependence of the degree of decomposition (α) on the time $t/t_{0.5}$ calculated for solid state reaction and experimental data for the dehydration of uranyl fumarate dihydrate: ○) open pan, X) sealed cups (low pressure), •) sealed cups (medium pressure).

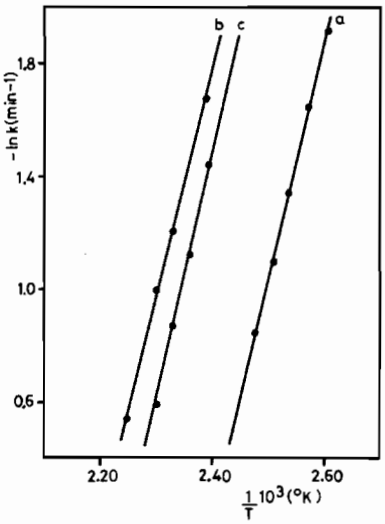


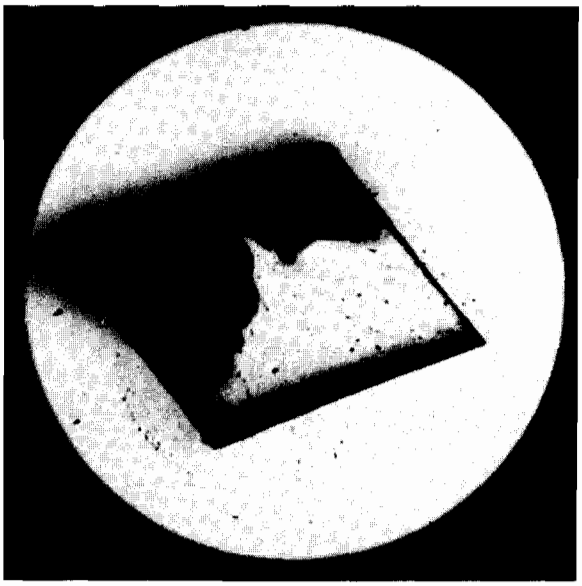
Fig. 2. Arrhenius plots for the dehydration of uranyl fumarate dihydrate: a) open pan, b) sealed cups (medium pressure), c) sealed cups (low pressure).

1 G. Bombieri, F. Benetollo, R. M. Rojas, M. L. de Paz and A. del Pra, *Inorg. Chim. Acta, 61*, 149 (1982).

TABLE I. Temperatures and Kinetic Parameters for the Isothermal Dehydrations of Uranyl Fumarate Dihydrate.

Experimental conditions	Temperatures of the isothermal heatings (°)	Final compound	F(α)	E(kcal mol^{-1})	A (s^{-1})
Open pan	110, 115, 120, 125, 130	anhydrous uranyl fumarate	A_2	16.46	2.2×10^{10}
Sealed cups (low pressure	145, 150, 155, 160	uranyl fumarate hemihydrate	A_3	20.03	4.3×10^{11}
Sealed cups (medium pressure)	145, 155, 160, 170	uranyl fumarate monohydrate	A_3	16.57	5.1×10^{9}

(a)



(b)

Fig. 3. Micrographs (X340) of partially dehydrated crystals of uranyl fumarate dihydrate heated a) at 110 °C for 8 minutes (open pan), b) at 145 °C for 8 minutes (sealed cups).

2 J. H. Sharp, G. W. Brindley and B. N. Narahari Achar, *J. Am. Ceram. Soc., 49*, 379 (1966).
3 J. D. Hancock and J. H. Sharp, *J. Am. Ceram. Soc., 55*, 74 (1972).

D23

Influence of Simulated Waste Oxides on the Durability of a Borosilicate Glass

G. CALESTANI, E. FERRAGUTI, A. MONTENERO*
Istituto di Strutturistica Chimica, Università di Parma, Italy
G. INGLETTO
Istituto di Biochimica, Medicina Veterinaria, Università di Parma, Italy
and M. BETTINELLI
Istituto di Chimica Generale, Università di Padova, Padua, Italy

Although the numerous papers on the chemical durability of nuclear waste glasses, more work is needed to understand the effects of waste oxides on the glass durability. This is due to the great variety of possible compositions and to the wide leaching conditions [1].

We have prepared the N. 189 glass (England), B, to which we have added 10% and 20% of SrO, Cs_2O, U_3O_8. Furthermore we studied the effects on B of an addition of 4% ZnO [2]. All the glasses were grounded and passed through 40 and 60 mesh sieves to obtain approximately the same surface for the same weight. Powders were leached by water at 70 °C for times varying from 1 day to 24 days and the solutions were analyzed by means of conventional methods.

TABLE I.

	SiO_2	B_2O_3	Li_2O	Na_2O	SrO	Cn_2O	U_3O_4	ZnO	Loss%
B	55.5	29.2	5.0	10.3	–	–	–	–	72.9
SR1	50.4	26.6	4.5	8.4	8.1	–	–	–	83.1
SR2	46.2	24.3	4.2	8.6	16.7	–	–	–	87.7
CS1	50.4	26.5	4.6	9.4	–	9.1	–	–	91.7
CS2	46.2	24.3	4.2	8.6	–	16.7	–	–	97.1
U1	50.4	26.6	4.5	9.4	–	–	9.1	–	73.5
U2	46.2	24.3	4.2	8.6	–	–	16.7	–	75.9
ZN4	53.3	28.0	4.8	9.8	–	–	–	4.0	15.3

In Table I are reported the sample compositions and the percentage of mass leached out after 24 days. In any case the waste ions make poorer the base glass with a maximum for the cesium containing glass. On the contrary the zinc ions, even if in a very low amount, allow very increased resistance to the corrosion [3].

As example in Figs. 1 and 2 are reported the quantitites of SiO_2 and Na species leached out in the course of the experiment.

It must be pointed out that the zinc containing glass continues to dissolve in an appreciable way. This is due to the fact that after 24 days the glass mass is