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Gamma irradiation effects on the thermal decomposition induction period in uranyl acetate

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Abstract

The effect of pre-irradiation with γ-ray prior to thermal decomposition on the induction period of dehydrated uranyl acetate has been investigated. The results indicated that the induction period of the investigated salt is shortened by exposure to γ-irradiation. Specifically, the induction period, I, is related to the radiation dose ϕ as $I = C_1 - C_2 \log \phi$, where C_1 and C_2 are constants. It is concluded that pre-exposure to ionizing radiation increases the number of nuclei that are active in salt breakdown in direct proportion to the γ-dose to which the sample had previously been exposed.

Keywords: Gamma Irradiation; Induction period

1. Introduction

Most often, studies on irradiated materials were performed with the aim to investigate whether radiation can modify one or more properties of the material in an important way. For example, irradiation may introduce lattice defects or trapped charges which can modify any subsequently measured process, such as thermal stability. Detailed descriptions of the kinetics of isothermal chemical decomposition are available in the literature [1,2]. It was, therefore, of interest to investigate whether the known relationship between the isothermal induction period I and radiation dose ϕ,

$$I = C_1 - C_2 \log \phi$$

where C_1 and C_2 are constants derived for the thermal decomposition of γ-irradiation inorganic solids [3–7], is applicable to uranyl acetate. No study of this type has been undertaken for this compound so far.

2. Experimental

Uranyl acetate dihydrate was obtained commercially (BDH, England) and used without further purification. The sample used for investigation was dried at 200°C in a muffle furnace to ensure complete dehydration. Isothermal kinetic studies of salt decomposition were completed using isothermal TG techniques as described in our earlier work [8]. Samples of dehydrated uranyl acetate were encapsulated, under vacuum, in glass vials and thereafter subjected to irradiation with different doses using Co60 γ-ray cell (220 Nordion INT-INC, Ontario, Canada) at a dose rate of 10^4 Gy/h. The source was calibrated making

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use of fricke ferrous sulphate dosimeter using 15.5 as the G-value for ferric ion production [9].

3. Results and discussion

Fig. 1 shows α vs. time plots for the isothermal decomposition, at 593 K, of four samples of dehydrated uranyl acetate, where α is the fraction decomposed at time t. Three of these samples had been subjected to γ-dose, ranging from 10^3 to 10^7 Gy together with comparative data for the un-irradiated salt. The figure show clearly that pre-irradiation of dehydrated uranyl acetate did not change the shape of the α vs. time curves for subsequent thermal decomposition of dehydrated uranyl acetate. Accordingly, pre-irradiation does not change the kinetics of propagation and growth of the decomposition centres which has been shown to proceed by a nucleation and growth mechanism (Avrami–Erofeev equation with $n = 3$) both, for un-irradiated and pre-γ-irradiated samples of uranyl acetate. Quantitative comparisons were made between the shapes of the α vs. time plots obtained for the un-irradiated salt and for two relatively highly irradiated samples (10^4 and 10^7 Gy). This comparison is shown in Fig. 2, where time values for the more rapid reactions of the irradiated samples have been appropriately scaled and the induction periods (discussed below) adjusted suitably to permit close juxtaposition of the three sets of data. The coincidence of the curves throughout their lengths is relatively good and we, therefore, confirm that the characteristic shape of the α vs. time decomposition curve did not change perceptibly by pre-irradiation in the $0.05<\alpha<0.95$ range.

The results plotted in Fig. 1 also show that the induction period of the γ-irradiated samples at the given decomposition temperature appears to be

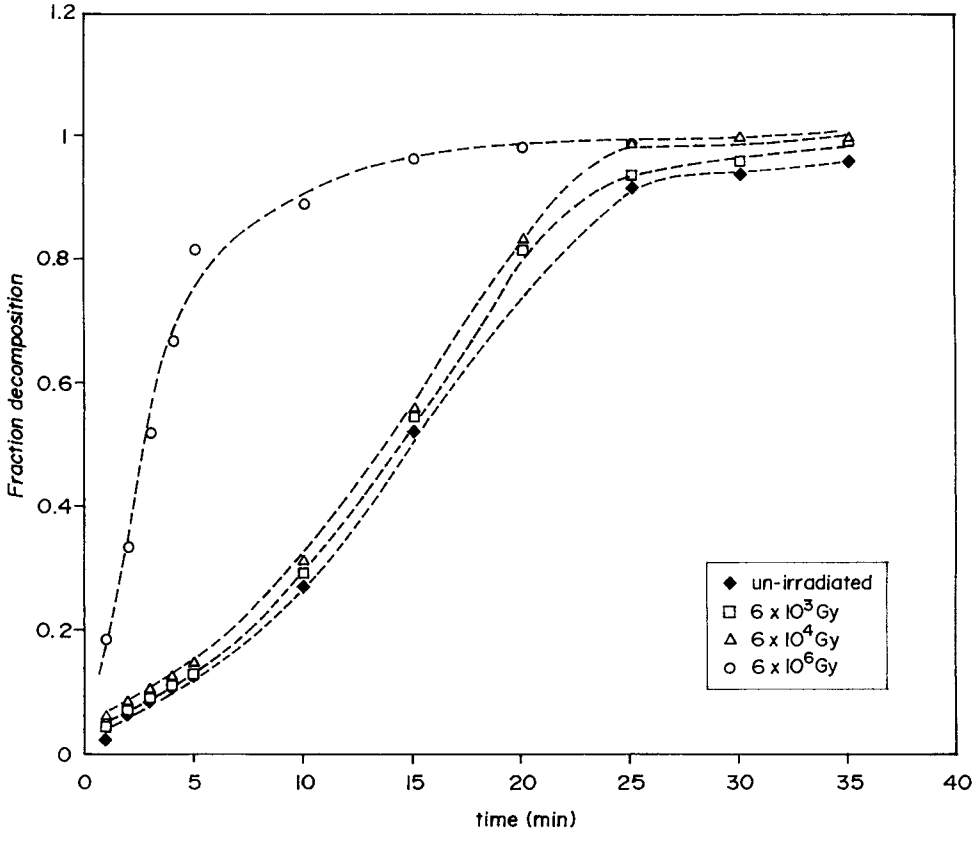

Fig. 1. Fractional decomposition α vs. time curves for the isothermal decomposition, at 320°C, of four samples of uranyl acetate.

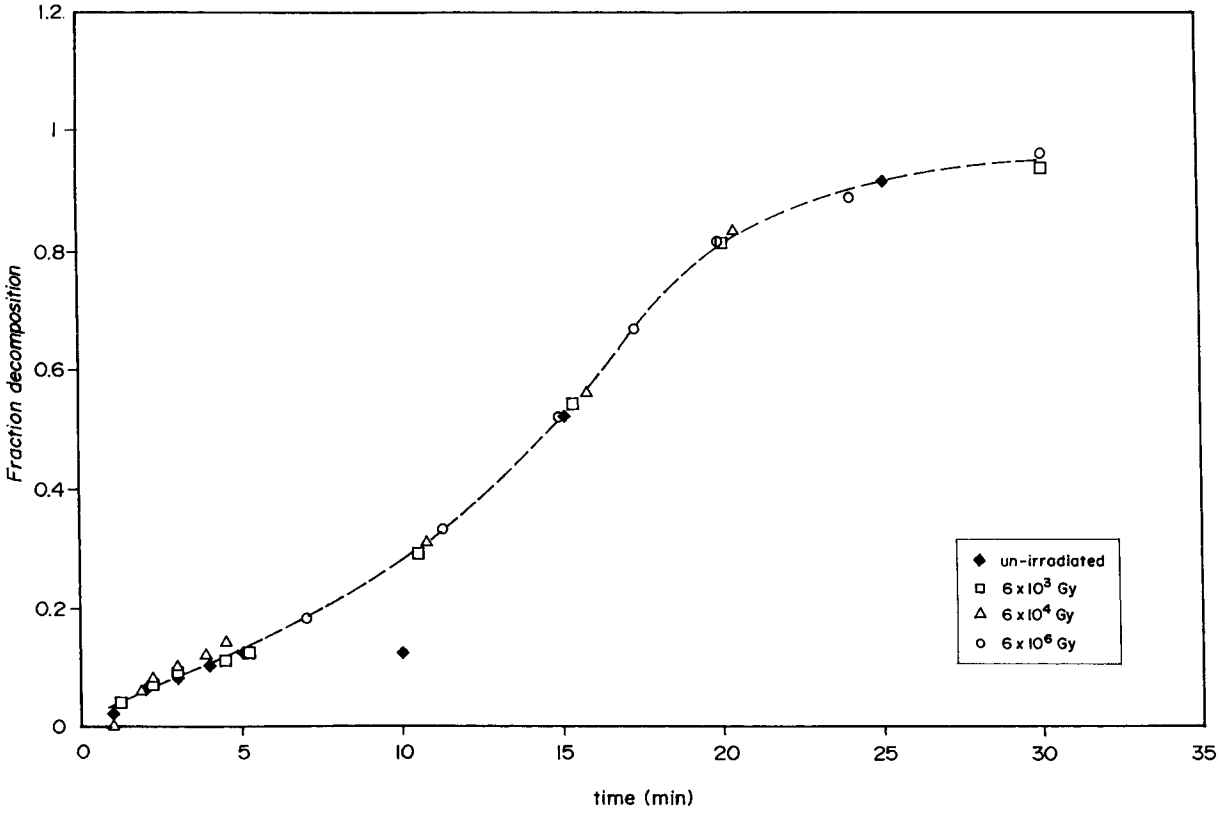

Fig. 2. Competitive decomposition curve, at 320°C, of four samples of uranyl acetate.

systematically reduced with γ-ray dose absorbed by the sample. Specifically, the induction period was related to the γ-dose as follows:

$$I = C_1 - C_2 \log \phi \quad (1)$$

where I is the induction period, i.e. it is the value of time corresponding to the end of induction period or the onset of the acceleratory period for samples that had previously been subjected to a total dose (ϕ), C_1 and C_2 refer to constants in the various I vs. ϕ equations [10]. Fig. 3 shows I vs. $\log \phi$ plots for the investigated dehydrated uranyl acetate.

3.1. Induction period

The induction period includes the initial slow processes, which subsequently culminate in the establishment of the growth interface that is the active participant in the main nucleation-and-growth reaction. The changes, through which the reactive precursors to nucleus development are converted into active zones, are slow before the autocatalytic properties of the developed nuclei are fully realized. These nucleation precursors may be identified as intrinsic imperfections in the reactant or radiation damage to the crystals. We conclude that similar, if not identical, kinetic processes result in the transformation of both type of precursors into growth nuclei.

The nature of the steps by which intrinsic or radiation-induced imperfections are converted into identical growth nuclei have not been characterized, but presumably include the following. Firstly, there may be slow changes at the ionic level, in which individual components of the crystal in the immediate vicinity of the imperfection interact to evolve a minute product grouping, possibly even a single or a small cluster of a few uranium atoms. Secondly, the early growth of such a small germ nucleus may be slower than that

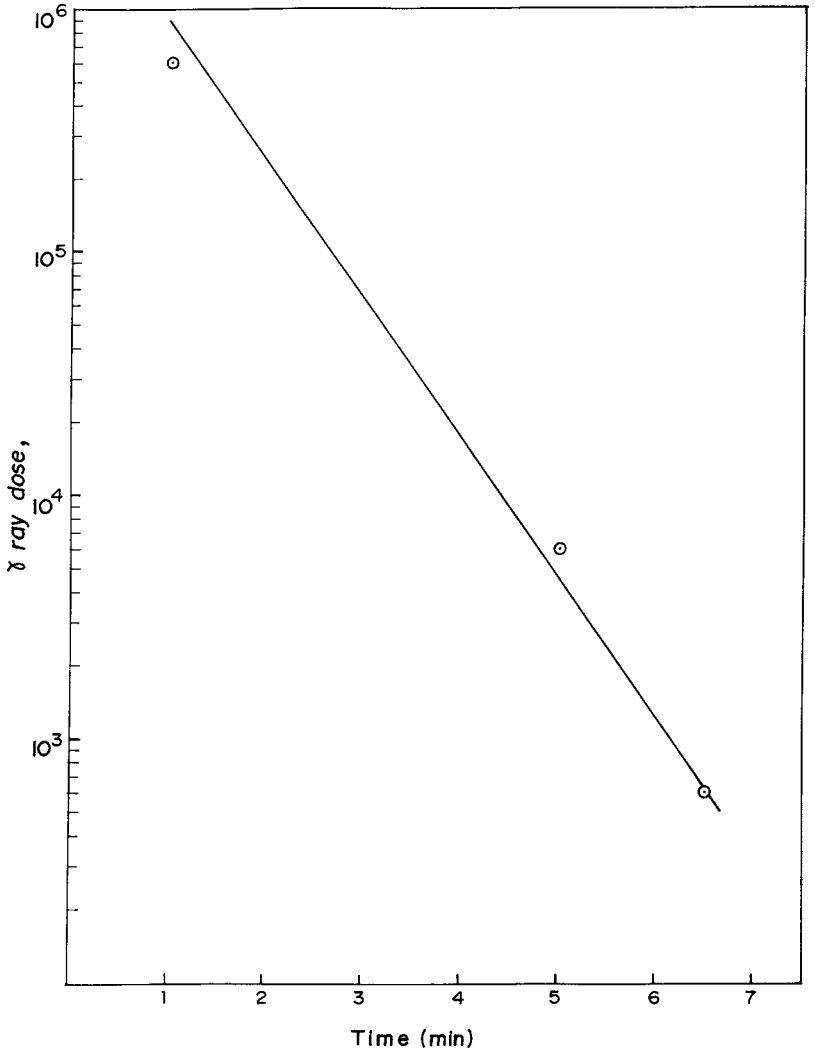

Fig. 3. Induction period I vs. total dose ϕ for uranyl acetate.

attained later; the properties of such small assemblages of uranium atoms can be expected to be different from those of larger metallic crystals.

The induction period in nucleation-and-growth reactions is not an unambiguous term and may be defined in several alternative, but equally acceptable ways. For the present purpose, we identify t_i as the time required for the precursors to generate the nuclei that will be henceforth transformed into fully active growth nuclei. This is identified here as the time interval prior to conforming with the Avrami–Erofeev equation.

The extended irradiation reduced the I values, that is to say the radiation evidently advanced the chemical changes through which the precursor sites were transformed into growth nuclei, as was observed experimentally from the decrease in the extent of induction period un increasing the γ-ray dose applied [11].

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