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Note

Influence of an ultraviolet pre-irradation on the thermolysis of uranyl formate

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Numerous researches have been devoted to the influence of a preliminary UV or γ irradiation on thermal decomposition, for instance of silver oxalate[1, 2], uranyl oxalate[3], lead formate[4], aluminium hydride[5] oxalato complex salts[6].

These researches are technically important in the field of thermal development of non-silver light sensitive solids and the word "photothermography" has been coined in order to term these processes[7].

For all previous instances, except for lead formate, it has been observed that pre-irradiation increases the thermolysis rate without changing its activation energy.

For uranyl formate monohydrate, photolysis[8, 9] and thermolysis[10] have been studied separately in our laboratory. The former study showed that submitted to radiations of wavelength shorter than 490 nm, corresponding to the first electronically excited state of uranyl ion[11], uranyl formate monohydrate undergoes a photolysis which at first transforms uranium^{VI} into uranium^{V}, with evolution of CO_2. The final solid photoproduct is a salt of uranium^{IV}, most probably UO(OH) HCOO[12]. Intermediate radicals have been detected by E.S.R. during the course of photolysis, and have been ascribed to $HCOO^{\cdot}$ and $HCO^{\cdot}$[9].

When heated, uranyl formate monohydrate first loses its hydration water and later undergoes a decarboxylation in three steps:

(1) $UO_2(HCOO)_2 \rightarrow UO_3 + HCOOH + CO$

(2) $HCOOH \rightarrow CO + H_2O$

(3) $x\,CO + UO_3 \rightarrow x\,CO_2 + UO_{3-x}$

The global kinetics of thermolysis, as determined by weight loss, obeys the Prout-Tompkins law with an activation energy equal to 39 ± 2 kcal mol^{-1}.

The purpose of the present work is to link these previous studies in investigating a possible "photothermographic" effect for uranyl formate.

EXPERIMENTAL

We used an electronic thermobalance Sartorius 4102 connected with a conventional vacuum set-up. The temperature is measured in a well located in the immediate vicinity of the sample. The starting material is uranyl formate monohydrate prepared after Sahoo et al.[13]. It can be dehydrated "in situ" by heating under vacuum at 150°C. Preirradiation is carried out by illuminating the monohydrate during 5 min with a mercury vapour lamp Philips HPK 125. Under these conditions, the solid absorbs about $2 \cdot 10^{-6}$ einstein. Unless otherwise stated, thermolysis is made under the pressure of the decomposition gases not condensed in a trap at 77 K (essentially CO).

RESULTS AND DISCUSSION

Figure 1 allows to compare the thermogravimetric recordings of the non-irradiated (dashed line) and pre-irradiated (solid line) samples. The heating rate was 1.2°C min^{-1} in both cases. It can be seen that preirradiation slightly inhibits the dehydration, but accelerates the decarboxylation.

Isothermal thermogravimetries have been performed on the anhydrous salt in the temperature range 260–310°C. As shown by Fig. 2, we check the validity of the Prout-Tompkins law both for the non-irradiated (dashed line) and for the pre-

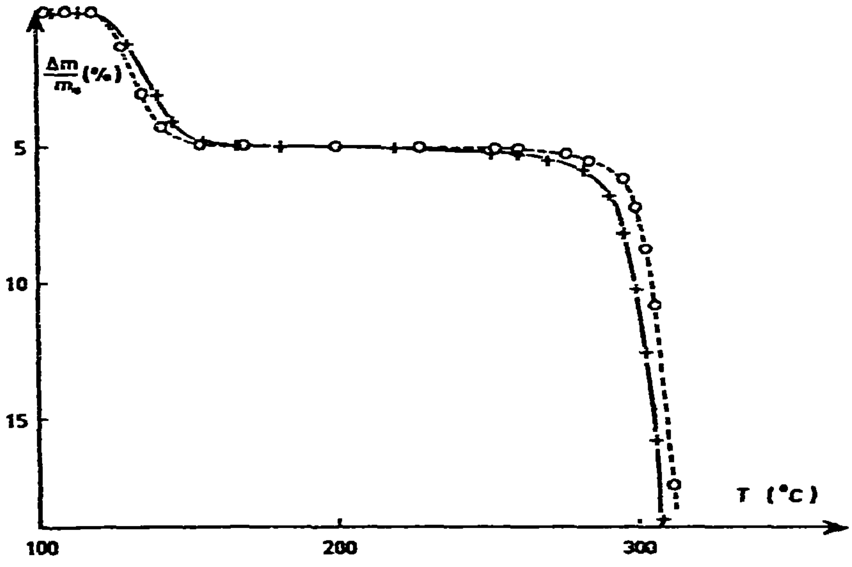

Fig. 1. Relative weight loss of $UO_2(HCOO)_2 \cdot H_2O$. ------, Non-irradiated; ——, after a 5-min UV irradiation.

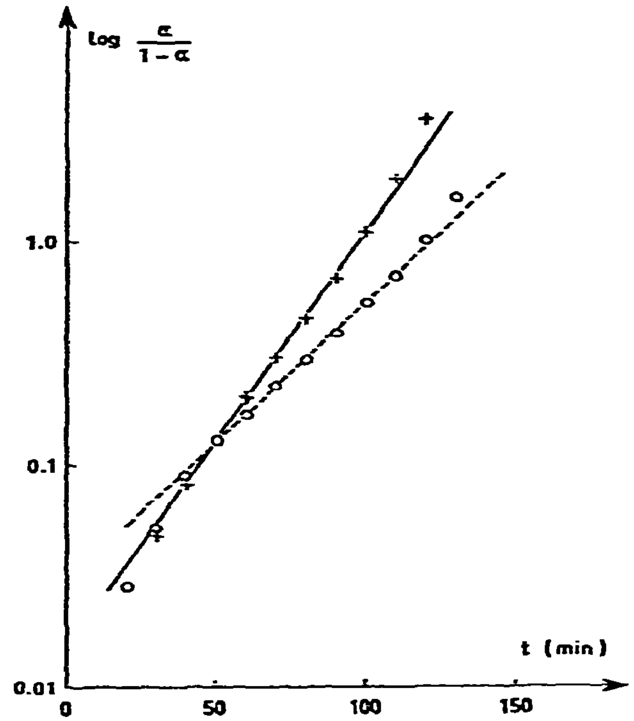

Fig. 2. Check of the Prout–Tompkins law. α, degree of decarboxylation; t, time. ------, Non-irradiated sample; ——, pre-irradiated sample.

irradiated (solid line) samples. Figure 3 shows that the rate constant k (slope of the preceding straight lines) is about 1.5 times higher in the latter case than in the former, but with an activation energy which remains the same.

This finding leads us to suppose that pre-irradiation does not change the mechanism of thermolysis, but simply increases the number of nuclei from which the process of branched chain nucleation usually underlying the Prout-Tompkins law, can take place. Owing to the temperature range in which the photothermographic effect is observed, the most likely candidates for these nuclei are U^{IV} ions coming from the thermal evolution of photochemically produced U^{V} ions. As we have previously shown[14] these latter ions are completely transformed into the former after 40 min at 85°C. The question is now which is the step of thermolysis in which U^{IV} ions can act as nuclei. The most likely is reaction (3) which is a reduction of U^{VI}. This reduction has been proved during the decarboxylation of uranyl formate in our experimental conditions by thermomagnetic studies[15]. An experimental finding which supports this assumption is the fact that when thermolysis is made under vacuum, pre-irradiation has no longer any influence on its kinetics. This can be explained by the fact that CO has a much shorter contact time with the solid, thus reducing reaction (3) to a much lesser extent. It has indeed been shown[10] that the final oxide is much less reduced under vacuum than under the pressure of the decomposition gases.

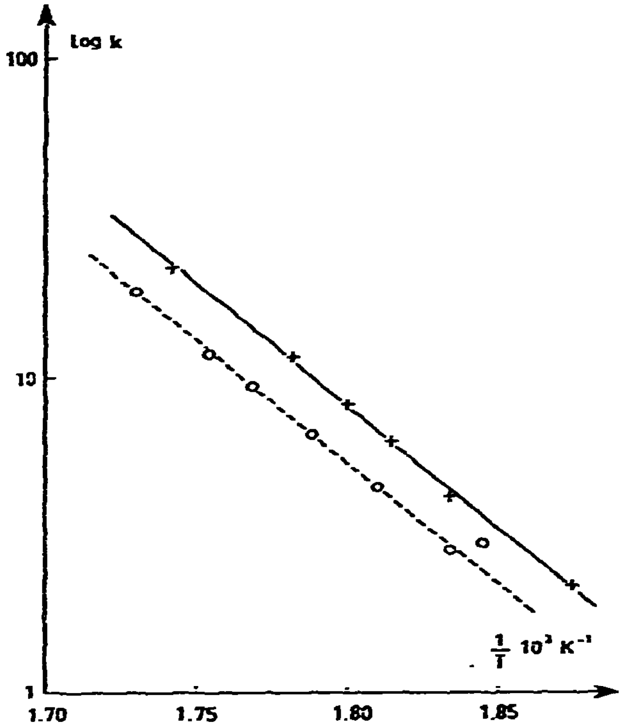

Fig. 3. Arrhenius plot. *k*, slope of the straight lines of Fig. 2. -----, Non irradiated sample; ——, pre-irradiated sample.

Finally, the U^{IV} ions photochemically created play the accelerating role which has been recognized for the final product of many thermolyses (e.g., that of ThO_2 in the thermal decomposition of thorium formate[16]).

Although this hypothesis is not the only one which can be thought of, the intervention of less stable species (like organic radicals) is less probable than that of U^{IV}, and the creation of physical defects (vacancies, dislocations) seems specific of a pre-irradiation with γ rays[1].

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