

**KINETICAL POSSIBILITIES OF CONTROLLED
TRANSFORMATION RATE THERMAL ANALYSIS (CRTA)
Application to the thermolysis of hexahydrated uranyl nitrate**

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In the first part, this paper reviews several ways to derive kinetical results from Controlled transformation Rate Thermal Analysis (CRTA) experiments: applying the rate-jump method to measure the activation energy, determining the reaction mechanism simply from the shape of the curve and finally deriving both the activation energy and the reaction mechanism from a single CRTA experiment. Application to the 5 steps of the thermal analysis of $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2 \cdot 4\text{H}_2\text{O}$ shows that the layered structure of the hydrate leads to 4 dehydration steps essentially following a mechanism of nucleation and 2-dimensional growth whereas the denitration step seems to be controlled by a double mechanism of diffusion and desorption. The first 4 water molecules to leave are in the same starting state but evolve in 2 steps, well separated by CRTA and involving 3 and 1 molecule, respectively, which is understood by structural considerations.

Previous work [1, 2] has demonstrated the efficiency of Controlled transformation Rate Thermal Analysis (CRTA) [3] for separating the successive steps of the dehydration and denitration of hexahydrated uranyl nitrate $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2 \cdot 4\text{H}_2\text{O}$. The "separating power" or "resolution" of CRTA first results from the possibility of controlling the rate of transformation at such a low rate - if needed - that the remaining temperature and pressure gradients through the sample are themselves low enough to avoid any overlapping of the successive steps. We have shown that in the case of hexahydrated uranyl nitrate, the separation of 5 successive steps also needs a control of the gas pressure over the sample at a relatively low value, which is also possible with CRTA: the recording given in Fig. 1 was obtained with a constant pressure of $5 \cdot 10^{-2}$ mbar and a rate of transformation (from

hexahydrate to trioxide) of c. a. 10^{-2}h^{-1} (i. e. needing 100 hours to complete the transformation). This experiment was carried out by Controlled transformation Rate Evolved Gas Analysis making use of a quadrupolar gas analyser [4, 5].

Our aim is now to carry out the precise kinetical study of the 5 successive steps previously isolated, by determining both the apparent energy of activation and the mechanism of the reaction. We shall of course take advantage of CRTA by applying the rate-jump method [4, 5] to determine the energy of activation of the reaction and by comparing the experimental plots of degree of reaction α vs. temperature T with the theoretical plots derived from the usual mechanisms but with the assumption of a constant rate of reaction [7].

Methodology

Starting definitions and assumptions

Separation of steps. We know, from our previous analytical work [2] that each plateau corresponds to a different step of the reaction. The temporary pressure drop which is observed between 2 successive steps (and which may be seen in the pressure recording of Fig. 1) is an indication that one step is completed and that a steep temperature rise is needed to launch the next step at a similar rate. We take the start of the pressure drop as the final time t_f of the step and the start of the pressure rise as the starting time t_0 of the next step.

Degree of reaction. For each individual step one may define a dimensionless degree of reaction α equal to 0 at the start of the reaction (for $t = t_0$) and to 1 at the end (for $t = t_f$).

The corresponding rate of reaction $d\alpha/dt$ is expressed in h^{-1} (reciprocal of the time needed to complete the step). Since, in CRTA, we may keep that rate of reaction constant all over the step, we write:

$$\frac{d\alpha}{dt} = \frac{1}{t_f - t_0}$$

and, by integration:

$$\alpha = \frac{t - t_0}{t_f - t_0}$$

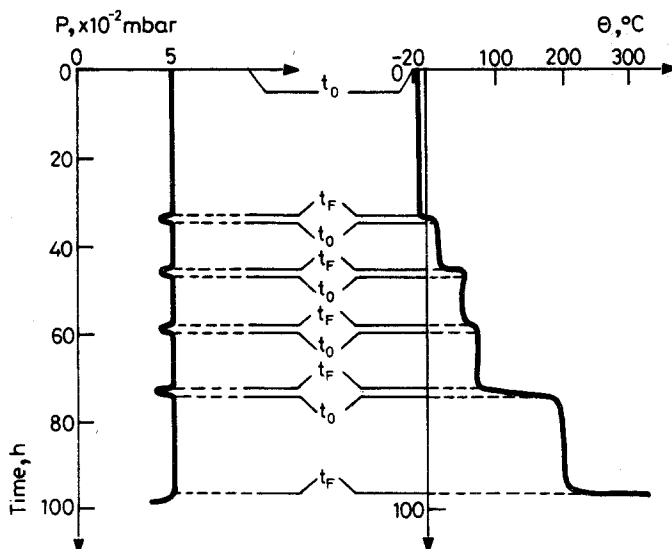


Fig. 1 Right: CTA trace of hexahydrated uranyl nitrate obtained under a residual pressure of $5 \cdot 10^{-2}$ mbar and a reaction rate of 10^{-2} h^{-1} . Left: simultaneous pressure recording showing transient pressure drops between 2 successive steps

which allows to convert the experimental curves of temperature vs. time obtained in our CTA-EGA experiments into α vs. temperature plots like those reported in Fig. 7. The rate of reaction is of course related to the degree of reaction through the function $f(\alpha)$ which depends on the reaction mechanism:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha)$$

where k is the rate constant.

We shall make use of the 10 $f(\alpha)$ functions listed by Sharp [8] for a number of reaction mechanisms involving boundary controlled reactions, random nucleation and growth of nuclei or diffusion controlled reactions (Table 1).

Arrhenius law. We shall process our experimental curves α vs. temperature by assuming that the Arrhenius law holds for each individual step, i. e.:

$$k = A \exp(-E/RT)$$

where A is an apparent pre-exponential factor, E is the molar apparent energy of activation (both A and E for a given step of the reaction), R is the molar gas constant and T is the thermodynamic temperature of the reaction.

Table 1 $f(\alpha)$ functions for the most common mechanisms in heterogeneous kinetics (from [8])

Mechanism	Symbol	$f(\alpha)$
Zero-order mechanism	R1	1
Phase boundary controlled reaction (contracting area)	R2	$(1-\alpha)^{1/2}$
Phase boundary controlled reaction (contracting volume)	R3	$(1-\alpha)^{2/3}$
Unimolecular decay law	F1	$(1-\alpha)$
2-dimensional random nucleation and growth of nuclei	A2	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$
3-dimensional random nucleation and growth of nuclei	A3	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$
One-dimensional diffusion (parabolic law)	D1	$1/2\alpha$
Two-dimensional diffusion	D2	$1/- \ln(1-\alpha)$
Three-dimensional diffusion (Jander equation)	D3	$\frac{3(1-\alpha)^{2/3}}{2[1-(1-\alpha)^{1/3}]}$
Three-dimensional diffusion (Ginstlein-Brounshtein equation)	D4	$\frac{3}{2\{(1-\alpha)^{-1/3}-1\}}$

Determining an activation energy by the rate-jump method

The principle of the method [6] is to bring the rate of reaction to swing between two preset values (with a ratio conveniently chosen as 1 to 3 or 1 to 4). The system which is operated following the CRTA mode, automatically responds by a swinging temperature, which is recorded (Fig. 2). Between 15 to 30 such jumps (and their corresponding drops) are usually performed to analyse one individual step. Each "tooth" of the temperature recording allows to determine a separate value of the activation energy, since it provides a couple of temperatures (one, T_2 , directly measured on the recording and the other, T_1 , obtained by extrapolation for exactly the same degree of reaction) and the corresponding couple of reaction rates (whose ratio "r" is known with a great accuracy, either because each rate may be kept constant as long as needed by a good calibration, or because the ratio is provided by a number of holes precisely drilled through two diaphragms giving access to the vacuum line and mounted in parallel). Since the degree of reaction remains virtually unchanged during the "rate-jump" and provided we assume that $f(\alpha)$ is not changed by the corresponding temperature jump (most often

in the 5 to 15 K range) we may say that the reaction rates (selected by the experimentalist) are in the same ratio as the rate constants, hence finally:

$$E = \frac{RT_1(\alpha)T_2(\alpha)}{T_2(\alpha) - T_1(\alpha)} \ln r$$

where T_1 and T_2 correspond to the same degree of reaction α . The interest of this method is at least fourfold:

- there is no need to know or to try any function $f(\alpha)$

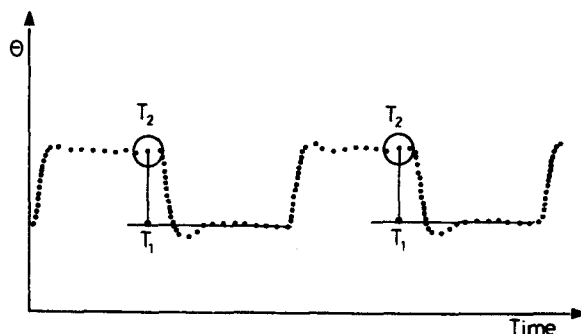


Fig. 2 CRTA trace corresponding to a rate-jump experiment to determine the activation energy

- the ratio r , as said above, is known precisely
- temperature, which is the only unknown, not only is an easy parameter to measure, but its value is here much more significant than in an experiment where the temperature gradients follow the fluctuations of the (uncontrolled) rate of reaction
- up to, say, 30 independent measurements may be successively carried out during one supposed step of the reaction: one may then check, a-posteriori, by comparing these values, if they are steady enough to support the use of the Arrhenius law and to confirm the existence of that individual step.

Let us finally point out that, like with any other experimental method, we access an apparent energy of activation (often different from method to method) whose meaning may be clarified in each case.

Determining the kinetic law from the α vs. T curves

The kinetic law may be determined by a graphical method, i. e. by comparing the experimental curves α vs. T with a set of theoretical curves which are built after assuming a given mechanism, selecting a numerical value for E (which we get from a rate-jump experiment, with no assumption about $f(\alpha)$) and for A (which we re-calculate, for each mechanism tried, for a given point of the α vs. T experimental curve).

The set of theoretical curves, as built by Criado and Ortega [7] may be easily split into 3 groups, simply after their general shape. It follows, as these authors point out, that the general shape of the experimental curve α vs. T obtained at constant reaction rate is in itself quite meaningful for the selection of the actual mechanism:

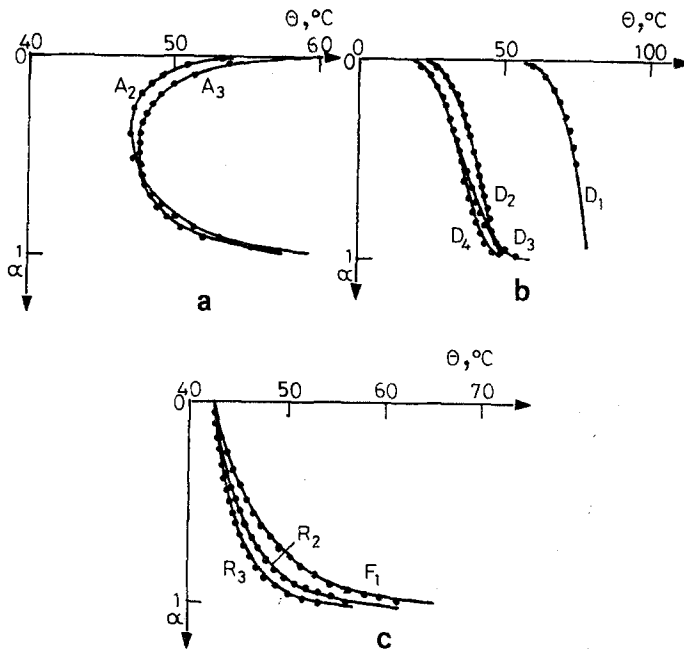


Fig. 3 Theoretical CRTA curves calculated for the 10 mechanisms listed in Table 1

- the mechanisms of nucleation and growth of nuclei (denoted A_2 and A_3 , respectively, in Fig. 3a) lead to curves with a temperature minimum (this being an interesting and special feature of the CRTA approach. By principle, one does not get of course such a temperature minimum neither by

conventional neither by "isothermal" thermal analysis). Moreover, the location of the minimum allows to determine whether the growth is two-dimensional (the minimum then theoretically takes place for $\alpha_m = 0.393$) or three-dimensional (then, theoretically, $\alpha_m = 0.487$);

- the mechanisms of diffusion denoted D_2 , D_3 and D_4 in Fig. 3b lead to curves with an inflexion point for a degree of reaction ranging from 0.40 and 0.65, whereas the unidimensional diffusion mechanism D_1 does not;

- the boundary controlled mechanisms (denoted R_2 and R_3) and also the mechanism corresponding to an order 1 (called by Sharp the "unimolecular" decay law [8]) give the same shape of curve (Fig. 3c) with no minimum nor inflexion point.

Determination of the mechanism and activation energy from one single CRTA experiment

Our approach is in some respect directly derived from Sharp's method [9] but with the simplification and increase in accuracy brought by CRTA. In Sharp's method, one plots $\ln \left(\frac{d\alpha/dt}{f(\alpha)} \right)$ vs. $1/T$ for various functions $f(\alpha)$ and looks for the best linear regression coefficient. The slope of this straight line and its ordinate at the origin provide the activation energy E and the pre-exponential factor A from the following equation:

$$\ln \left(\frac{d\alpha/dt}{f(\alpha)} \right) = \ln(A) - \frac{E}{RT} \quad (1)$$

Although with the convenience of being differential, this method suffers from the limited accuracy of the experimental determination of "instantaneous" reaction rates. This shortcoming completely vanishes in the case of a CRTA experiment, since the reaction rate is constant and may be known with a great accuracy. Moreover, Eq. (1) may now be simplified into:

$$\ln(f(\alpha)) = \ln\left(\frac{C}{A}\right) + \frac{E}{RT}$$

where C is the constant reaction rate, so that plots of $\ln(f(\alpha))$ vs. $1/T$ for various functions $f(\alpha)$ are theoretically enough to provide the kinetical law and activation energy from one single CRTA experiment.

Experimental results

Activation energies and enthalpies of reaction for the 5 steps of the thermal decomposition of hexahydrated uranyl nitrate

The rate-jump method for determining the energy of activation was applied a number of times to each of the 5 steps of the thermal decomposition. The corresponding recordings of temperature vs. time are reported in Fig. 4: Fig. 4a is related to the 1st step, i.e. to the loss of the 3 first water molecules, Figs 4b, 4c and 4d are related to the loss of the next 3 water molecules and Fig. 4e is related to the denitration step. The first step was carried out under a controlled residual pressure of 10^{-1} mbar (high enough to allow this step to take place, under our low reaction rate conditions, at a temperature not lower than -20°) and the next steps under a pressure of $5 \cdot 10^{-3}$ mbar. Even our highest reaction rate was always smaller than 0.01 h^{-1} . On top of each Fig. 4a to 4e the values of the activation energies derived from each rate jump are graphically reported. For one given step, these values are identical within 10 %, which a-posteriori supports the assumption that the Arrhenius law holds here for each individual step. To lighten the significance of these "apparent energies of activation" we tried to compare them with the corresponding enthalpies of reaction. The latter were measured with a Perkin-Elmer DSC-4 equipment, with argon flow at a heating rate of 1 deg/min. The DSC trace is reported in Fig. 5 and shows 5 endothermic peaks. If we assume that they correspond to the 5 steps of our CRTA experiment, we may compare, for each step, as in Table 2, the energy of activation (mean value from the set of successive rate-jump experiments shown in Fig. 4) and the enthalpy of reaction (mean value from two DSC experiments and derived with reference to 1 mole of starting hexahydrate). We don't report the enthalpy value for the 1st step, since we start the DSC run at room temperature, under a flow of dry argon which already initiates the dehydration before any heating. The enthalpy values for the 2nd and 3rd step are comparable to those given by Franklin and Flanagan [10], which are 56 and 76 $\text{kJ} \cdot \text{mol}^{-1}$, respectively, whereas our value for the 4th step is higher.

We found it interesting to make a graphical comparison of these enthalpies and activation energies, as is done in Fig. 6 where the starting (i.e. lowest) state is that of the trihydrate and where the successive enthalpies of reaction are added to each other. This representation shows that, for steps 2 to 4, the activation energy is nearly twice higher than the corresponding enthalpy, which may be understood by a mechanism where thermal energy is needed both to break the bonds and to distort the structure just enough to

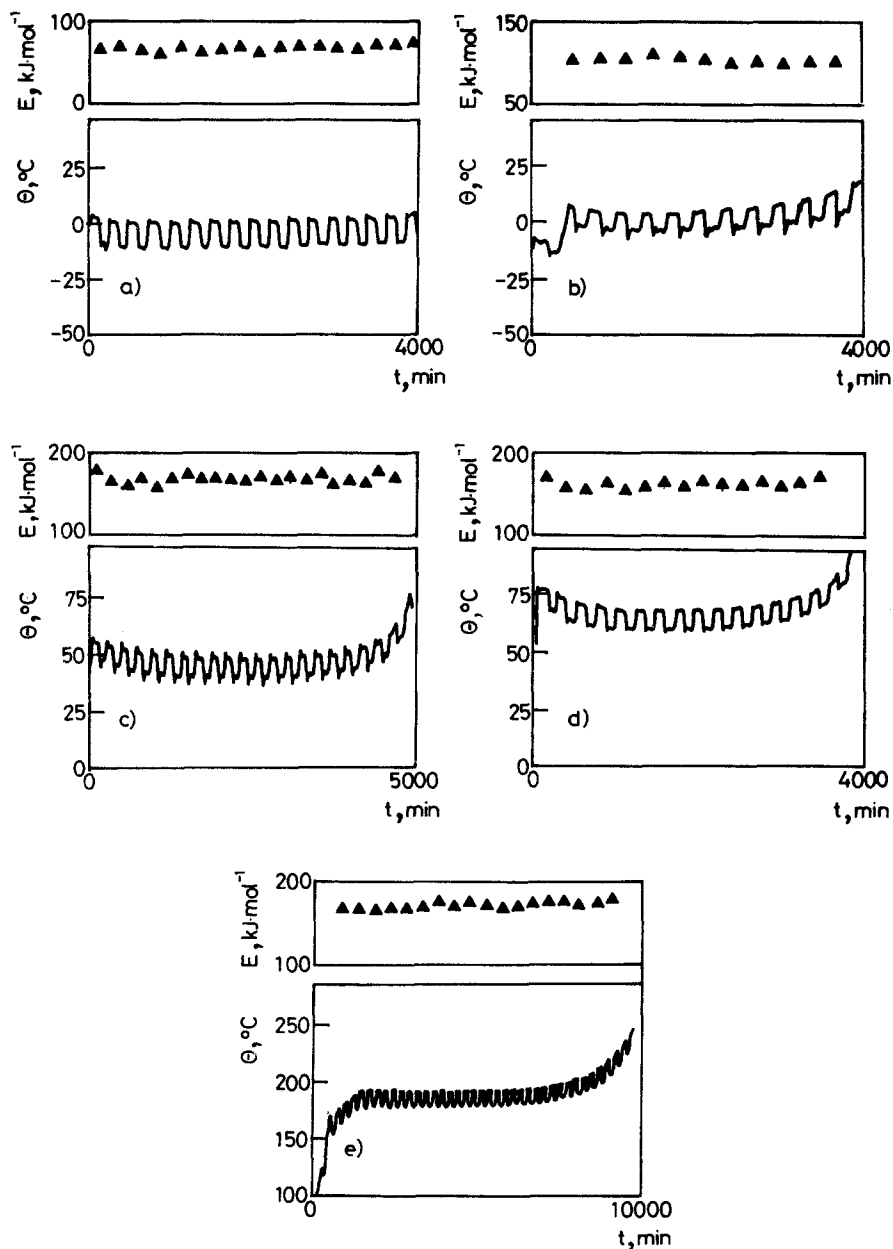


Fig. 4 CRYTA traces obtained when applying the rate-jump method to the 5 successive steps (a to e) of the thermolysis of $\text{UO}_2(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. The energies of activation derived from each rate-jump are indicated by a succession of points on top of each figure

allow the water molecules to go through. It may be noted that for the 3rd step the activation energy is even high enough to break the bonds of the last water molecule, although the latter only evolves during the following step. For the denitration step, the activation energy is only 14 % higher than the corresponding enthalpy.

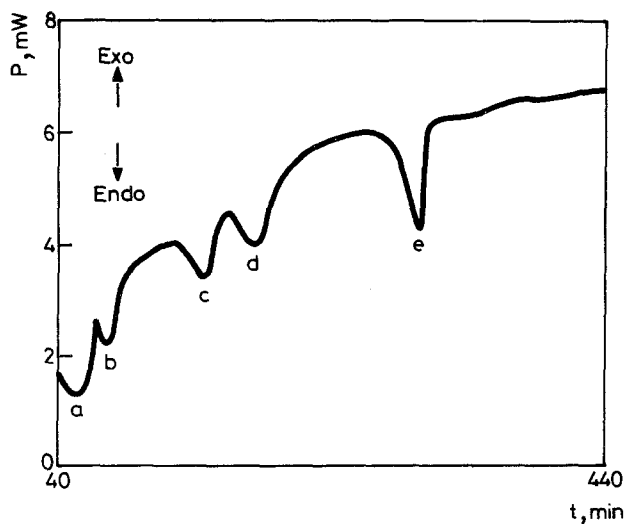


Fig. 5 DSC trace for 6.4 mg of hexahydrated uranyl nitrate. Heating rate: 1 deg min⁻¹

Table 2 Activation energies and corresponding enthalpies of reaction as measured for the various steps of the thermal analysis of $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_{2.4}\text{H}_2\text{O}$

	1 st step a	2 nd step b	3 rd step c	4 th step d	5 th step e
$\frac{E_a}{\text{kJ mol}^{-1}}$	71 ± 5	104 ± 8	171 ± 11	163 ± 9	171 ± 6
$\frac{\Delta H_m}{\text{kJ mol}^{-1}}$		50 ± 6	73 ± 2	89 ± 4	150 ± 6

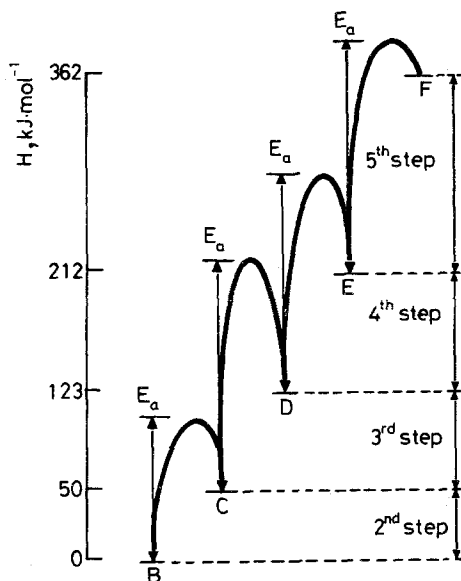


Fig. 6 Comparison of the enthalpy changes with the corresponding activation energies. Starting state (*B* level, taken as the origin for the enthalpy scale): $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$. Final state (*F* level): UO_3 . Dihydrate, Monohydrate and Anhydrous nitrate at levels *C*, *D* and *E*, respectively

Determination of the mechanism of the various steps from the shape of the CRTA curves

Our experimental CRTA traces (temperature vs. time) may be converted, for each step, into plots of degree of reaction α vs. temperature, as is done in Figs 7a to 7e. These CRTA experiments carried out with a Controlled transformation Rate EGA equipment in such a way that, for each step, it is the rate of production of one given gas (H_2O for steps 1 to 4, NO for step 5) which was controlled (by means of the quadrupole analyser) and kept constant (by means of the CRTA control loop acting on the heating of the furnace). On the same figures we have plotted a number of theoretical curves corresponding to the most probable mechanisms and to the values of E and A measured or calculated for the step under consideration.

Although the experimental curve of Fig. 7a shows a temperature minimum which could be explained by a mechanism of nucleation and growth of nuclei, that curve is somewhat flatter than the theoretical curves calculated for this mechanism (2-dimensional or 3-dimensional growth, although closer

to the former, from the location of the minimum). We may consider that the experimental curve actually lies between those above and between a vertical line which would be the theoretical curve for a mechanism controlled by a desorption step (shown to take place under reduced pressure [10]). In these

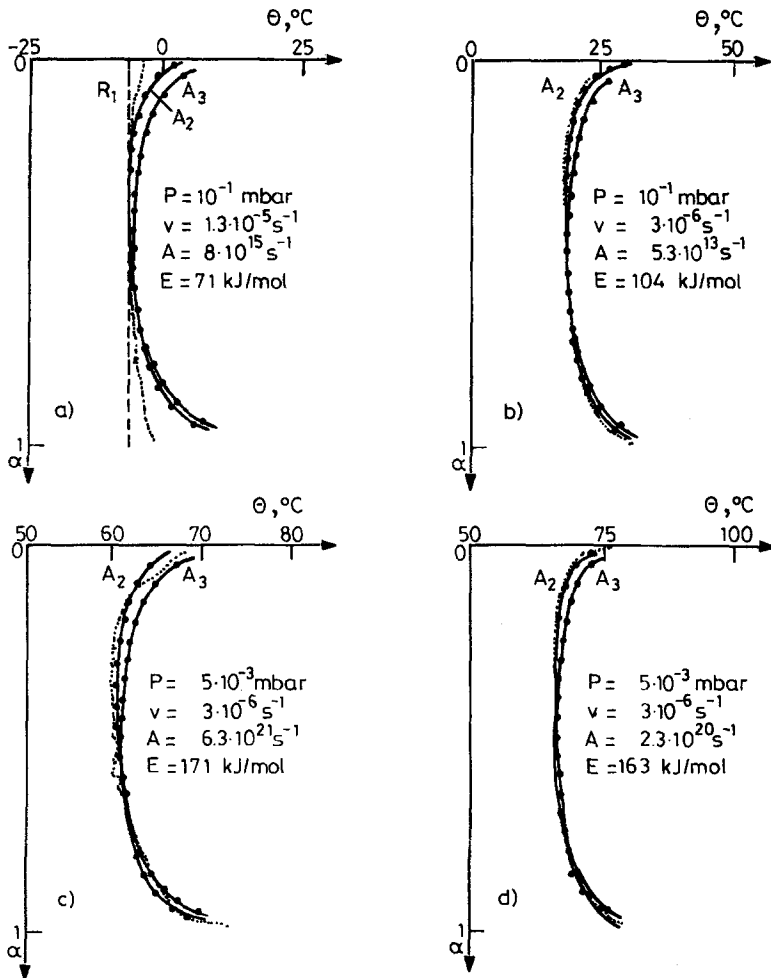


Fig. 7a-d Comparison of experimental (fine dots) and calculated CRTA curves for the first four steps (here, labelled a to d) of the thermolysis $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2 \cdot 4\text{H}_2\text{O}$. Steps a to d: calculation for a mechanism of nucleation and growth, either two-dimensional (A_2) or three-dimensional (A_3)

conditions it is likely that both mechanisms take place here and lead to a "mixed" apparent energy of activation.

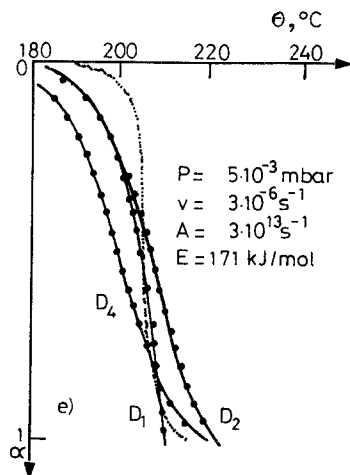


Fig. 7e Comparison of experimental (fine dots) and calculated CRTA curves for the fifth step of the thermolysis $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2 \cdot 4\text{H}_2\text{O}$. Thermolysis of calculation for a mechanism of diffusion, either mono (D_1), two (D_2) or three (D_4) dimensional

For the next 3 steps (Figs 7b to 7d), the fit is quite satisfactory between the experimental curve and that calculated with the assumption of nucleation and 2-dimensional growth of nuclei (using in the calculation the activation energy obtained independently from the rate-jump experiments).

Finally, the experimental curve corresponding to the denitration step (Fig. 7e) has an inflexion point indicating the existence of a diffusion mechanism, possibly superimposed with a desorption one, since neither mechanism D_1 , D_2 nor D_4 give a satisfactory fit.

Data processing from one single CRTA experiment

Plotting the experimental data as $\ln(f(\alpha))$ vs. $1/T$ and comparing them with the theoretical curves shows that the best fit - although not fine - is obtained for the nucleation and growth of nuclei, which is consistent, even if less clear, with the conclusions of the preceding section. Nevertheless, the activation energies derived are much higher than those previously determined, i.e. here 200 to 300 $\text{kJ}\cdot\text{mol}^{-1}$ for the 1st step and 100 to 200 $\text{kJ}\cdot\text{mol}^{-1}$

for the other steps. The explanation of such a discrepancy may lie in the fact that 1 % error on α may produce - as a simple calculation shows - up to 10 % error on E . Obtaining the required precision on α may need the addition of a thermobalance to the EGA equipment [11].

Structural understanding of the thermolysis

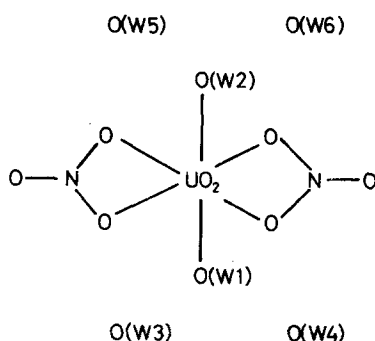


Fig. 8 Molecular structure of $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2 \cdot 4\text{H}_2\text{O}$ with water molecules O(W1) to O(W6)

The crystal structure of uranyl nitrate hexahydrate has been determined by both X-ray and neutron diffraction [12, 13]. These two structural studies have shown the compound to be correctly formulated $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2 \cdot 4\text{H}_2\text{O}$. Indeed, two nitrate groups acting as bidentate ligands and two water molecules coordinated in a plane perpendicular to the uranyl group, feature a di-nitrato, di-aqua, di-oxo-uranium complex represented in Fig. 8. Whereas two unidentate water molecules (O(W1) and O(W2)) belong to the environment of the 8-coordinate uranium atom, the other four molecules of hydration (O(W3) to O(W6)) are not associated with the metal atom but involved in a loose hydrogen-bonding system which binds the various units of the structure into a continuous lattice. More precisely, O(W1) and O(W2) are engaged in a triangular coordination whereas O(W3) to O(W6) water oxygen atoms are surrounded by an approximately tetrahedral arrangement of hydrogen atoms. In Fig. 9, we report a tridimensional view of the crystal structure showing the free water molecules between the discrete $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$ moieties. The requirement of efficient lattice packing leads, for this quasi-planar complex (the uranyl oxygen atoms apart) to a

herringbone stacking arrangement along the crystallographic b axis. Moreover the water molecules out of the uranium sphere of coordination form infinite sheets perpendicular to the crystallographic a axis and parallel to the basal planes (darkened in Fig. 9) which are containing the uranyl moiety and bisecting the nitrate groups. This seems to corroborate our kinetical study proposing a germination and bidimensional nucleation mechanism. Although the four O(W3) to O(W6) water molecules are activated in a similar manner, the activation induces a structural modification able to trap one of the four molecules which provides an adequate molecular packing for the structure of the resulting product i. e. uranyl nitrate trihydrate.

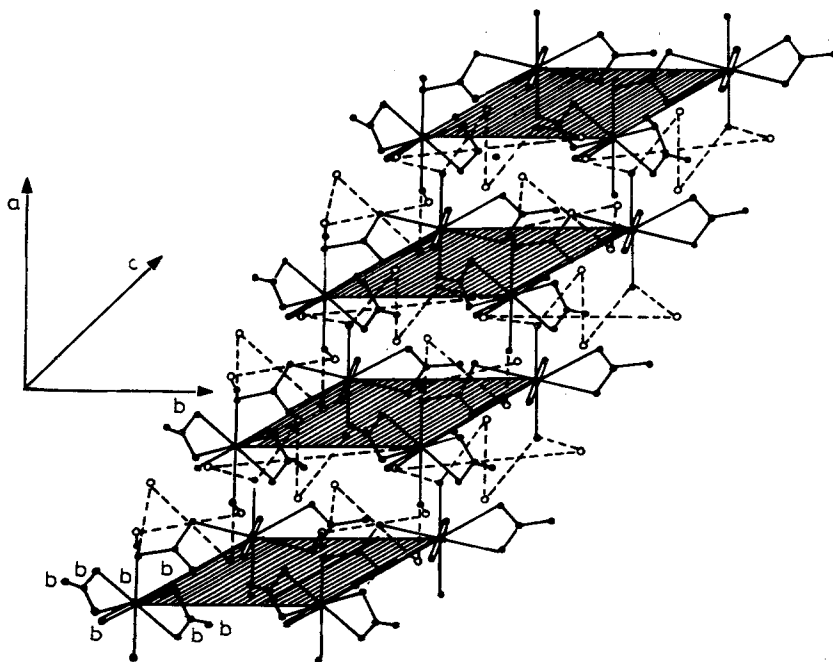


Fig. 9 Layered structure of $\text{UO}_2(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. - Atom and water molecules making up the basic "butterfly" pattern of the dihydrate; \circ Other water molecules: "b" atoms are those in the basal plane of the hexahydrate structure

To avoid studying the diffusion of water through a powder bed instead of the dehydration of uranyl nitrate hexahydrate, Moseley and Seabrook [14] have analyzed the kinetics of decomposition for single-crystal specimens.

Since they did not observe any anisotropic effect due to the layers of water molecules, they concluded that water loss and subsequent recrystallisation into the trihydrate crystal structure does not take place along any particular crystallographic direction. Our thermogravimetric analysis, at low pressure and with a controlled low rate of decomposition, differs to a certain extent from the experimental followed by these authors, so that different results are not unexpected. None of the four water molecules is indeed crystallographically unique, so that it is reasonable to think that they are submitted to the same packing forces and consequently are energetically equivalent. It therefore seems plausible that in an aleatory manner one of them remains in the lattice and is available for the crystallisation of the trihydrate. Although extensive unpacking and repacking occurs at the phase transition, so that no relationship is to be found between the orientations of the units cells of the two phases, no bonds are cleaved in the $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$ moiety. The fourth water molecule remains free, interspersed between the di-nitrato, di-aqua, di-oxo-uranium complexes, naturally in sheets, so that its departure involves the same type of nucleation and 2-dimensional germination mechanism as the previous molecules. In this conditions, it is not unexpected that Dalley, Mueller and Simonson [15] find for the nitrate dihydrate the same sphere of coordination for uranium as that formerly found in the nitrate trihydrate [16] and hexahydrate [12, 13].

The structure of the dihydrate belongs to the monoclinic system and, as shown in Fig. 10, the four formula weights in the unit cell are located on special position 2a and 2b of space group $P2_1/c$, resulting in two crystallographic independent molecules I and II, at $0,0,0/0,1/2,1/2$ and $1/2,0,0/1/2,1/2,1/2$, respectively. Contrary to the hydrogen atoms of molecule I, not involved in hydrogen-bonding, the hydrogen atoms of molecule II participate in two different hydrogen bonds with the terminal nitrate oxygen of a molecule I and an uranyl oxygen atom of another molecule II. The two water molecules of II consequently account for the packing of the basic structural units and the existence of two types of molecule I and II may explain a thermal decomposition of the dihydrate in two steps via an uranyl nitrate monohydrate. Planes of water molecules, perpendicular to the crystallographic *a* axis, are of course, hypothetical but potential decomposition planes for a two dimensional mechanism of dehydration.

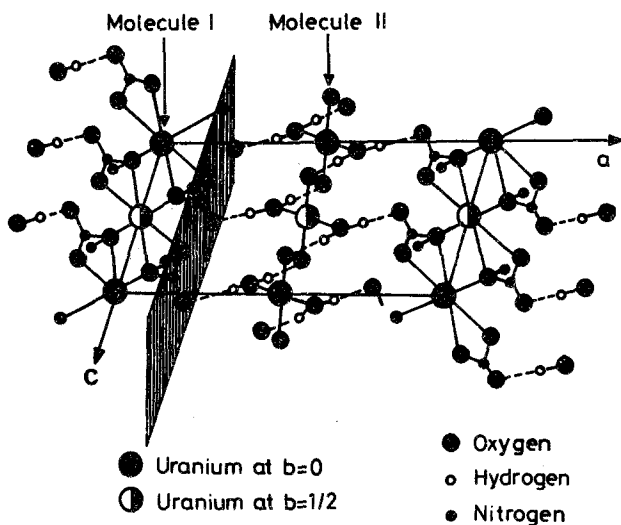


Fig. 10 Molecular structure of the dihydrate, after [13]

Conclusions

A few conclusions are worth being drawn, in our opinion, from the preceding work, i.e.:

The rate-jump method results in a unique point by point analysis of the course of a thermal decomposition, as shown by Fig. 4 where more than 100 successive, independent and "assumptionless" measurements of the apparent activation energy are reported.

Applying this method allows to check, a posteriori, the relevance of the Arrhenius law to the step studied: for a given mechanism, the apparent energy of activation must remain independent from the degree of reaction.

Simply examining the shape of the α vs. temperature curve obtained in a CRTA experiment is a quite efficient means to determine the reaction mechanism; moreover, in the case of our uranyl nitrate hexahydrate sample, for 3 steps among 5 the fit of the theoretical and experimental curves is such that it virtually eliminates any residual uncertainty (cf. Figs 7b to 7d).

In that hexahydrate, 4 water molecules with the same starting structural state leave in 2 successive steps, well separated by CRTA and involving 3 and 1 water molecules, respectively.

In the dihydrate, although both water molecules of a given $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$ moiety are identical, the existence of 2 different types of such moieties gives rise, here again, to 2 successive steps.

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Zusammenfassung — Diese Arbeit gibt einen Überblick über einige Verfahren zur Erstellung kinetischer Ergebnisse aus CRTA-Experimenten (Controlled transformation Rate Thermal Analysis): Anwendung des rate-jump-Verfahrens zur Messung der Aktivierungsenergie, Ermittlung des Reaktionsmechanismus lediglich aus der Kurvenform und letztlich die Ermittlung der Aktivierungsenergie und des Reaktionsmechanismus aus einem einzigen CRTA-Experiment. Eine Anwendung auf die 5 Schritte der thermischen Zersetzung von $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2 \cdot 4\text{H}_2\text{O}$ zeigt, daß die Schichtenstruktur des Hydrates zu 4 Dehydratationsschritten führt, denen im wesentlichen ein Mechanismus aus Keimbildung und 2-dimensionalem Wachstum zugrundeliegt, während der Denitratationsschritt durch einen Doppelmechanismus aus Diffusion und Desorption bestimmt zu sein scheint. Die ersten 4 Wassermoleküle befinden sich im selben Ausgangszustand, werden aber in 2 Schritten abgegeben, mittels CRTA als 3+1 Moleküle separat beobachtbar, was mittels struktureller Überlegungen verstanden werden kann.