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KINETICS OF THERMAL DEHYDRATION AND DECOMPOSITION OF Zr^{IV} AND UO_2^{II} COMPLEXES OF 2′,4′-DIHYDROXYCHALKONE

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ABSTRACT

The mechanisms of the dehydration and decomposition of the complexes $Zr(C_{15}H_{11}O_3)_4 \cdot 2H_2O$ and $UO_2(C_{15}H_{11}O_3)_4 \cdot 2H_2O$ are reported, together with the determination of the kinetic parameters, Z, E and $\Delta S^{\star}$, by non-isothermal methods. The complexes dehydrate and decompose in three well-defined steps involving a random nucleation mechanism. The first step involves dehydration and the second and third the loss of the ligand moiety. The intermediates formed undergo further decomposition remaining unstable over a considerable range of temperature.

INTRODUCTION

The complexes have already been prepared and characterised [1] and the present study deals only with the mechanism of decomposition and the evaluation of the kinetic parameters.

EXPERIMENTAL

The complexes were heated at the rate of 10°C min^{-1} using a Paulik–Paulik MOM derivatograph (Hungary) [2] for recording the simultaneous DTA–DTG and TG curves of the complexes. Non-isothermal methods (Piloyan–Novikova [3], Coats–Redfern [4] and Horowitz–Metzger [5]) were employed for the analysis of the thermogravimetric data and for establishing the mechanism of dehydration. The plot of $\alpha - T(K)$ was also analysed to support the mechanism of dehydration.

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RESULTS AND DISCUSSION

The $Zr(C_{15}H_{11}O_3)_4 \cdot 2H_2O$ complex (Fig. 1) starts decomposing at 363 K and continues up to 453 K when a break in the DTA curve is observed

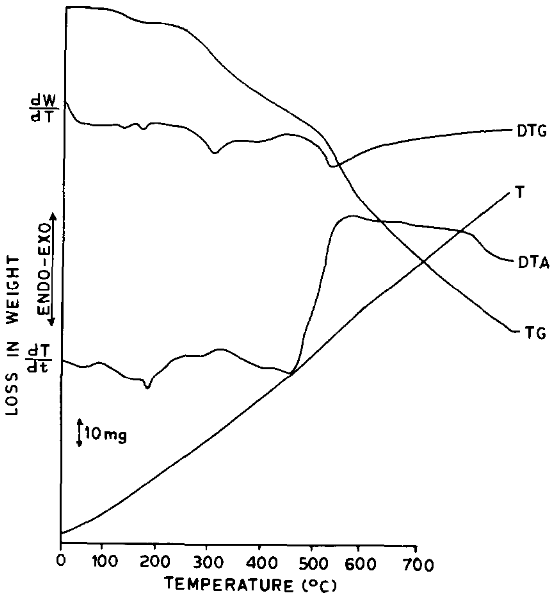

Fig 1. Simultaneous DTG–DTA–TG curves of $Zr(C_{15}H_{11}O_3)_4 \cdot 2H_2O$.

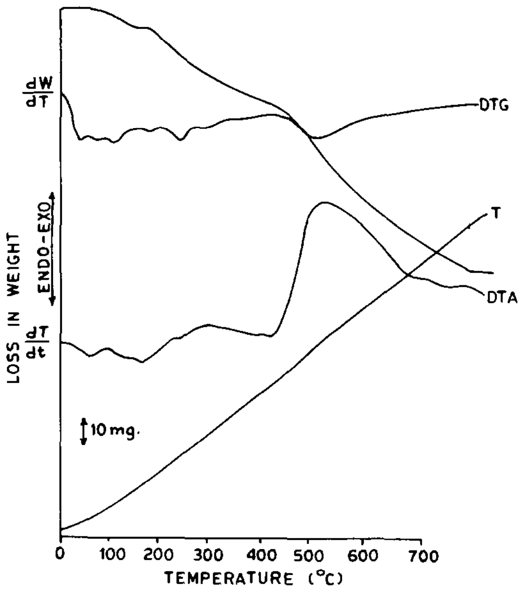

Fig. 2. Simultaneous DTG–DTA–TG curves of $UO_2(C_{15}H_{11}O_3)_2 \cdot 2H_2O$.

TABLE 1

Non-isothermal kinetic studies of the dehydration of the complexes

Complex	Step	Equation	E (kJ mol^{-1})	Z (s^{-1})	ΔS^* (J K^{-1} mol^{-1})	Model [a]
$Zr(C_{15}H_{11}O_3)_4 \cdot 2H_2O$	First	Piloyan–Novikova	51.69	15.68×10^3	−72.29	–
	Second	Piloyan–Novikova	55.52	111.33	−91.84	–
$UO_2(C_{15}H_{11}O_3)_2 \cdot 2H_2O$	First	Piloyan–Novikova	31.24	26.10	−95.41	–
	Second	Piloyan–Novikova	52.65	152.58	−90.70	–
$Zr(C_{15}H_{11}O_3)_4 \cdot 2H_2O$	First	Coats–Redfern	54.70	37.16×10^3	−69.17	R.N.
	Second	Coats–Redfern	25.53	2.3396	−105.79	R.N.
$UO_2(C_{15}H_{11}O_3)_2 \cdot 2H_2O$	First	Coats–Redfern	41.24	865.83	−82.77	R.N.
	Second	Coats–Redfern	28.72	0.501	−111.22	R.N.
$Zr(C_{15}H_{11}O_3)_4 \cdot 2H_2O$	First	Horowitz–Metzger	53.28	8.033×10^{-3}	−124.59	R.N.
	Second	Horowitz–Metzger	39.54	2.309×10^{-3}	−130.78	R.N.
$UO_2(C_{15}H_{11}O_3)_2 \cdot 2H_2O$	First	Horowitz–Metzger	44.85	7.083×10^{-3}	−125.06	R.N.
	Second	Horowitz–Metzger	31.43	1.970×10^{-3}	−131.21	R.N.

[a] R.N., Random nucleation mechanism.

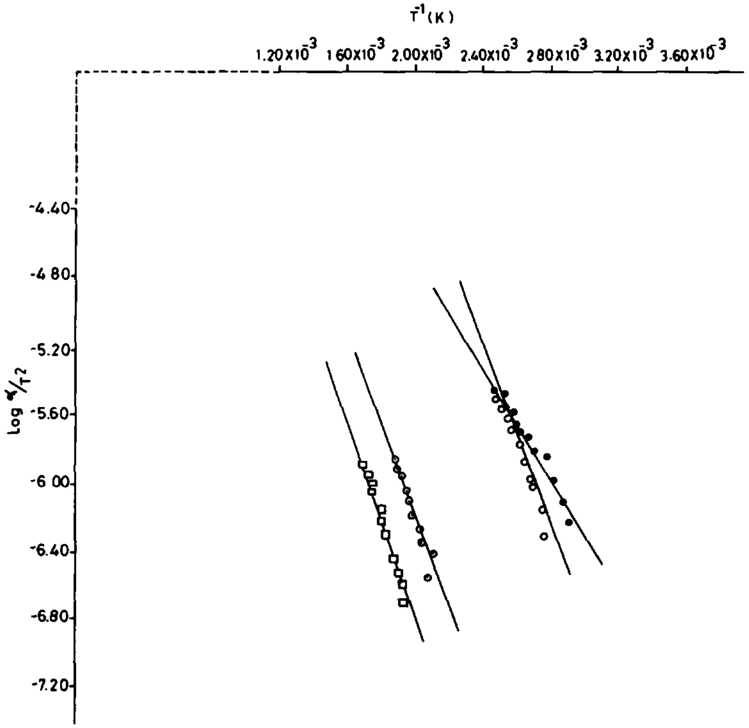

Fig. 3. Piloyan–Novikova plots. Zr^{IV} complex: ○, 1st step; □, 2nd step. UO_2^{II} complex: ●, 1st step; ⊙, 2nd step.

corresponding to the loss of two coordinated water molecules. The next phase of the decomposition occurs between 463 K and 773 K, corresponding to the loss of the phenyl ring of the ligand. Between 773 K and 1473 K the complex loses the ligand moiety completely. Beyond this temperature, no weight loss is observed as the stable oxide ZrO_2 is formed.

Similarly, for $UO_2(C_{15}H_{11}O_3)_2 \cdot 2H_2O$ (Fig. 2), the decomposition ranges 373–463 K and 483–1473 K correspond respectively to the loss of coordinated water molecules and the ligand moiety. There is no further loss in weight beyond 1473 K because the stable oxide U_3O_8 is formed as the end product.

Table 1 summarises the non-isothermal kinetic studies of the dehydration of the complexes, the values of the kinetic parameters and the mechanism of decomposition.

The fractional weight loss (α) and the corresponding $(1-\alpha)^n$ values are calculated from the TG curves (Figs. 1 and 2) at different temperatures during the first two steps of decomposition, where n depends upon the reaction model. The plots of log α/T^2 against T^{-1} (Fig. 3), $\log\{-[\ln(1-\alpha)]/T^2\}$ against T^{-1} (Fig. 4) and $\log[-\ln(1-\alpha)]$ against θ (Fig. 5) for the Piloyan–Novikova, Coats–Redfern and Horowitz–Metzger methods respec-

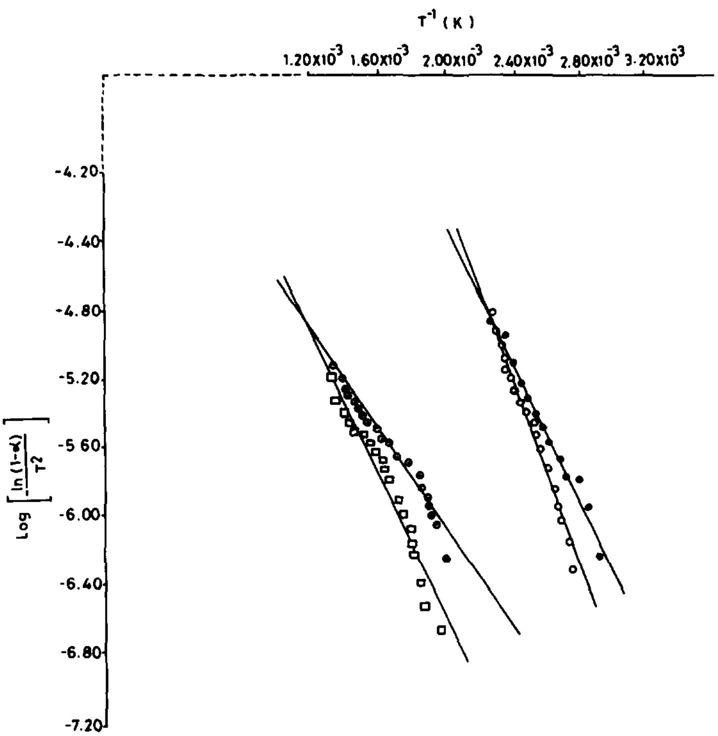

Fig. 4. Coats–Redfern plots. Zr^{IV} complex: ○, 1st step; □, 2nd step. UO_2^{II} complex: ●, 1st step; ⊙, 2nd step.

tively were found to be the best linear fits, where $\theta = T - T_m$, T_m being the peak temperature. The Coats–Redfern and Horowitz–Metzger graphs suggest a random nucleation mechanism. The plot of α against T(K) (Fig. 6) also suggests this mechanism for the dehydration and decomposition [6] of the complexes. The α–T(K) curves constructed on the basis of TG data for the first two steps of decomposition of both the complexes are of the same pattern. The curves begin with an acceleratory period without any apparent induction period, which indicates that no surface nucleation or branching occurs before the start of these steps [7].

The values of slope, intercept and energy of activation (E) are obtained from the graphs (Figs. 3–5). The values of the intercept and the energy of activation are substituted in eqn. (1) for evaluating the values of Z in case of the Piloyan–Novikova and Coats–Redfern methods, while the values of Z in the Horowitz–Metzger method were calculated by using eqn. (2). The entropies of activation ($\Delta S^{\star}$) were calculated using eqn. (3)

$$\text{Intercept} = \log \frac{ZB}{\beta E} \qquad (1)$$

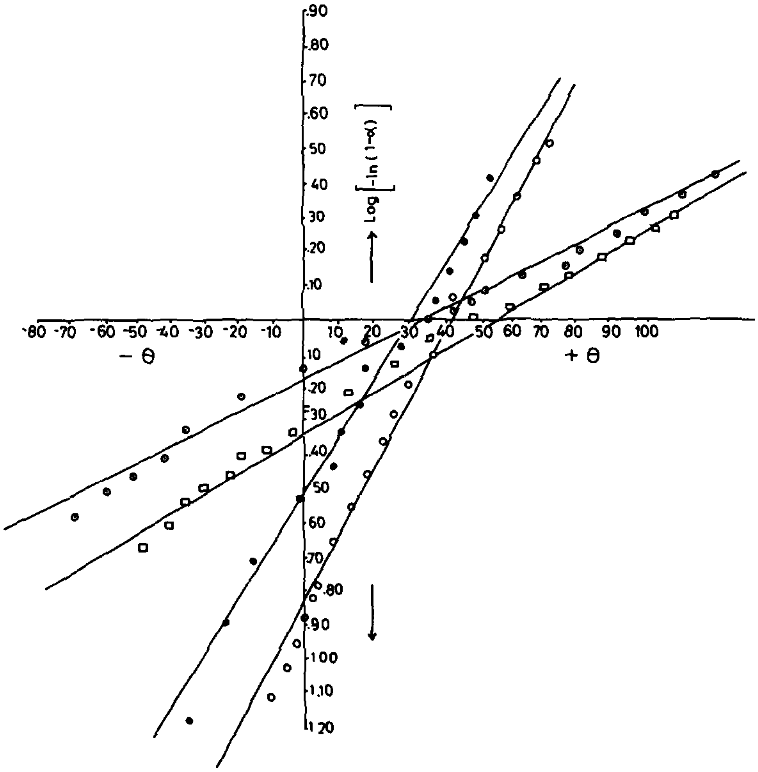

Fig. 5. Horowitz–Metzger plots. Zr^{IV} complex: ○, 1st step; □, 2nd step. UO_2^{II} complex: ●, 1st step; ⊙, 2nd step.

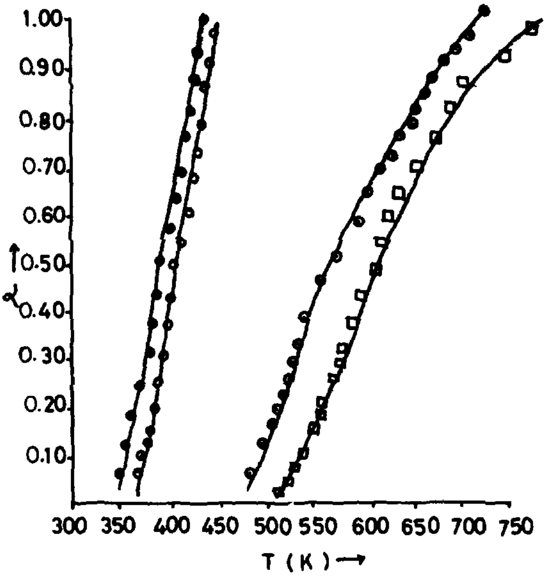

Fig. 6. α–T(K) plot. Zr^{IV} complex: ○, 1st step; □, 2nd step. UO_2^{II} complex: ●, 1st step; ⊙, 2nd step.

$$Z = \frac{E}{RT_m}\beta \exp\left(\frac{E}{RT_m^2}\right) \tag{2}$$

$$Z = \frac{kT_m}{h}\exp\left(\frac{\Delta S^\star}{R}\right) \tag{3}$$

where R is the molar gas constant, β the rate of heating (K s^{-1}), k the Boltzmann constant and h Planck's constant.

It is concluded that the complexes undergo dehydration in the first step of decomposition. The next two steps involve the loss of the ligand moiety. The oxides, ZrO_2 and U_3O_8, are formed as the end products. Both the dehydration·and decomposition involve random nucleation mechanisms.

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