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Note

ON THE THERMAL STABILITY OF Fe^{III} AND Ho^{III} HYDRATED GLUCONATES

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The authors report their results concerning the thermal decomposition of Fe^{III} and Ho^{III} gluconates

INTRODUCTION

Following our research concerning solid–gas decompositions [1] this paper deals with a thermoanalytical investigation of $Fe(gluc) \cdot 4H_2O$ and $Ho(gluc)_2 \cdot 6H_2O$

EXPERIMENTAL

Powders of $Fe(gluc) \cdot 4H_2O$ and $Ho(gluc)_2 \cdot 6H_2O$, where gluc is gluconic acid rest, were synthesised according to the method described elsewhere [2]

To record the heating curves TG, T, DTG, and DTA a Q-1500-D-(MOM, Budapest) Paulik–Paulik–Erdey derivatograph was used The powder X-ray diffractograms were recorded with a Philips (PW-1400) diffractometer using chromium K_α radiation The heating curves were recorded at heating rates between 2 5 K min^{-1} and 10 K min^{-1} in a static air atmosphere and, in some cases, in flowing argon To record the heating curves in argon, a O D 103 (MOM, Budapest) Paulik–Paulik–Erdey derivatograph was used

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For the kinetically possible reactions, the non-isothermal kinetic parameters were estimated using the Coats–Redfern [3] method The experimental data were automatically analysed on a TI 66 computer using an original program [4]

RESULTS AND DISCUSSION

The X-ray diffractograms did not exhibit any distinct lines, thus showing an amorphous state of both compounds used in this investigation

The thermal decomposition of Fe(gluc) 4H$_2$O

According to the heating curves, the decomposition occurs via the following steps

$$\mathrm{Fe(gluc)\ 4H_2O_{(s)}} \xrightarrow{338\ \mathrm{K}\ (2\ 5\ \mathrm{K\ min^{-1}})} \mathrm{Fe(gluc)\ 2H_2O_{(s)} + 2H_2O_{(g)}} \qquad \text{(I)}$$

where the temperature above the arrow corresponds to the maximum reaction rate As shown by the DTA curve, this is a normal endothermic decomposition At higher temperatures, the loss of the other two water molecules

$$\mathrm{Fe(gluc)\ 2H_2O_{(s)}} \xrightarrow{445\ \mathrm{K}\ (2\ 5\ \mathrm{K\ min^{-1}})} \mathrm{Fe(gluc)_{(s)} + 2H_2O_{(s)}} \qquad \text{(II)}$$

occurs simultaneously with the oxidative degradation on the gluconic rest, which explains the overall exothermicity shown by the DTA curve and the corresponding sharp weight change shown by the TG and DTG curves A third exothermic process, which we shall denote III, occurs at higher temperatures (with the maximum rate at 553 K) The values of nonisothermal kinetic parameters, reaction order n, activation energy E and pre-ex-

TABLE 1

Values of the non-isothermal kinetic parameters for reactions (I) and (III)

Reaction	Heating rate (K min^{-1})	n	E (cal mol^{-1})	A (s^{-1})	r [a]	k_T (s^{-1})	T (K)
I	10	1	9 100	$2\ 1\times10^3$	0 990	$3\ 23\times10^{-3}$	339
III	2 5	1	13 000	$3\ 5\times10^5$	0 994	$1\ 52\times10^{-3}$	339
III	10	1	16 000	$5\ 84\times10^3$	0 981	$4\ 11\times10^{-3}$	563
		2	24 200	$2\ 51\times10^7$	0 994	$1\ 19\times10^{-2}$	
III	2 5	1	21 500	$2\ 76\times10^6$	0 987	$1\ 36\times10^{-2}$	563
		2	14 300	$7\ 13\times10^2$	0 993	$2\ 13\times10^{-3}$	563

[a] The correlation coefficient of the Coats–Redfern linear plot

ponential factor A for the kinetically workable reactions I and III are given in Table 1

The values of the kinetic parameters obtained for step I at 2.5 K min^{-1} should be considered for at least two main reasons (1) the higher value of the correlation coefficient, and (2) the lower heating rate at which the kinetic parameters presumably remain unaltered by heating transfer phenomena For the same reasons the values $n = 2$, $E = 14\ 30$ kcal mol^{-1}, $A = 7\ 13 \times 10^2$ s^{-1} and $h_{563} = 2\ 13 \times 10^{-3}$ should be considered for reaction III In this case, i e $n = 2$, the values of the kinetic constant at 563 K for the heating rates used differ by a factor of approximately 5

The thermal decomposition of Ho(gluc)$_2$ 6H$_2$O

The first decomposition step occurs at heating rates between 2 5 K min^{-1} and 10 K min^{-1} according to the equation

$$\mathrm{Ho(gluc)_2\ 6H_2O_{(s)}} \xrightarrow{333\ \mathrm{K}\ (2\ 5\ \mathrm{K\ min^{-1}})} \mathrm{Ho(gluc)_2\ 2H_2O_{(s)} + 4H_2O_{(g)}} \qquad \text{(IV)}$$

According to the DTA curve, reaction IV is endothermic At higher temperatures, the shape of the TG, DTG and DTA curves change with the heating rate At a rate of 10 K min^{-1} between 411 K and 443 K, a sharp weight change is seen in the TG and DTG curves which corresponds to reaction V A more careful inspection of the DTG curve shows that reaction V is actually not simple but the result of two overlapping reactions As the DTA curve shows an exothermic peak, it can also be concluded that reaction V corresponds partially to the oxidative degradation of the ligand At higher temperatures, another process, VI, occurs. The maximum reaction rate of VI was recorded at 513 K. As shown by the DTG and DTA curves, this process is not simple either The last process, VIII, the maximum rate of which is recorded at 792 K, and which is strongly exothermic, is not simple In this process carbon dioxide is evolved

At lower heating rates (5 K min^{-1} and 2 5 K min^{-1}) reaction IV is followed by a single exothermic reaction, IX, with a maximum rate at 513 K (2 5 K min^{-1})

Reaction X, which is also exothermic, occurs with a maximum rate at 640 K (2 5 K min^{-1}) For the low heating rates used, the samples were heated up to 873 K, i e the temperature at which $\mathrm{Ho_2O(CO_3)_2}$ is obtained It must be emphasised that the TG curves in argon at a heating rate of 10 K min^{-1} are quite similar to those obtained at lower heating rates in static air atmosphere

The values of the non-isothermal kinetic parameters for the kinetically possible reactions which occur at the thermal decomposition of Ho(gluc)$_2$ 6H$_2$O are given in Table 2

TABLE 2

Values of the non-isothermal parameters for reactions IV, IX and X

Reaction	Heating rate (K min^{-1})	n	E (cal mol^{-1})	A (s^{-1})	r	k_T (s^{-1})	T (K)
IV	10	2	15 800	$4\ 61\times10^{7}$	0 996	$2\ 39\times10^{-3}$	333
IV	5	2	16 700	$8\ 15\times10^{7}$	0 994	$1\ 13\times10^{-3}$	333
IV	2 5	2	15 900	$5\ \ \times10^{7}$	0 996	$2\ 13\times10^{-3}$	333
IX	2 5	1	13 400	$5\ 72\times10^{2}$	0 997	$1\ 16\times10^{-3}$	513
X	5	2	23 300	$1\ 23\times10^{5}$	0 997	$1\ 49\times10^{-3}$	640
X	2 5	2	24 200	$1\ 79\times10^{5}$	0 996	$1\ 09\times10^{-3}$	640

As can be seen from the data given in Table 2, the values of the kinetic parameters do not change with heating rate

To facilitate the assignment of the high-temperature decomposition steps of Ho(gluc)$_2$ 6H$_2$O, the non-isothermal kinetic parameters of holmium carbonate decomposition were determined

According to the thermogravimetric data at 10 K min^{-1}, the decomposition occurs in three steps

$$\mathrm{Ho_2(CO_3)_3\ 4H_2O_{(s)}} \xrightarrow{393\ \mathrm{K}} \mathrm{Ho_2(CO_3)_{3(s)} + 4H_2O_{(g)}} \qquad \text{(XI)}$$

$$\mathrm{Ho_2(CO_3)_{3(s)}} \xrightarrow{653\ \mathrm{K}} \mathrm{Ho_2O_2CO_{3(s)} + 2CO_{2(g)}} \qquad \text{(XII)}$$

$$\mathrm{Ho_2O_2CO_{3(s)}} \xrightarrow{883\ \mathrm{K}} \mathrm{Ho_2O_{3(s)} + CO_{2(g)}} \qquad \text{(XIII)}$$

The values of the non-isothermal kinetic parameters for the kinetically possible reactions XI and XII are given in Table 3 Inspection of Tables 2 and 3 shows that the values of the kinetic constants for reactions X and XI occurring at quite close temperatures are comparable

TABLE 3

Values of the non-isothermal parameters for reactions XI and XII

Reaction	Heating rate (K min^{-1})	n	E (cal mol^{-1})	A (s^{-1})	r	k_T (s^{-1})	T (K)
XI	10	2	8 500	$1\ 49\times10^{2}$	0 999	$2\ 88\times10^{-3}$	393
XII	10	2	14 500	$8\ 6\ \ \times10^{1}$	0 987	$1\ 31\times10^{-3}$	653

CONCLUSIONS

From this study of the thermal stability of Fe^{III} and Ho^{III} hydrated gluconates the following conclusions were drawn

(1) The non-isothermal kinetic parameters have been evaluated for the kinetically possible decomposition steps

(2) The values of the non-isothermal kinetic parameters obtained for the decomposition of Fe^{III} gluconates are quite sensitive to heating rate

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