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SOLID STATE DECOMPOSITION STUDIES ON METAL SALICYLATES. KINETICS OF ISOTHERMAL DEHYDRATION OF SOME 5-SUBSTITUTED METAL SALICYLATO COMPLEXES

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ABSTRACT

The kinetics of the thermal dehydration of 5-substituted cadmium(II), manganese(II), nickel(II) and zinc(II) salicylato complexes have been studied by isothermal TG measurements applying the principal $g(\alpha)$ expressions ($0.1 \le \alpha \le 0.9$). Results show that for the halogen substituted complexes the dehydration rate increases in the order Mn > Ni > Cd > Zn, while for the nitro substituted complexes the order is Cd > Zn > Mn > Ni. The dehydration process seems to follow, most closely, a phase-boundary reaction mechanism. The values found for the activation energy of dehydration process are low compared with the experimental ΔH values.

The enthalpy values of all three decomposition stages of these compounds were determined by DSC for the hydrated 5-chlorosalicylato complexes with manganese(II), nickel(II) and zinc(II). These enthalpy values are compared with those determined for the corresponding unsubstituted metal salicylato complexes.

INTRODUCTION

Metal salicylate complexes, $M(Hsal)_n$ and $M(sal)_n$ (H_2sal denotes salicylic acid), have been investigated by a number of workers both in solution and in the crystalline state [1–6]. However, the complexation properties of substituted salicylic acids have been studied less extensively than those of unsubstituted salicylic acid. Melnik et al. [7,8] have reported thermal behaviour of copper(II) 5-chloro- and 5-bromosalicylate trihydrates.

In our earlier papers we have reported the thermal analysis and kinetics of some hydrated transition metal salicylato complexes [9–12]. We have also previously prepared, characterized and studied the thermal behaviour of 5-chloro-, 5-bromo-, 5-iodo- and 5-nitrosalicylato dihydrates with cadmium(II), manganese(II) and zinc(II), as well as the corresponding tetrahydrate complexes of nickel(II) [13,14]. As a continuation of this research we report investigations on the thermal stability and kinetics of isothermal dehydration of 5-chloro-, 5-bromo-, 5-iodo- and 5-nitrosubstituted cadmium(II), manganese(II), nickel(II) and zinc(II) salicylato complexes. In this work, our

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goal is to investigate the dependence of thermal stability and dehydration rate on temperature, substituent and metal ions of some transition metal salicylato complexes. The results are compared with those reported for the corresponding unsubstituted salicylato complexes [15]. In addition, DSC runs in the temperature range of 298–873 K were performed for the $Mn(5\text{-}ClHsal)_2 \cdot 2H_2O$, $Ni(5\text{-}ClHsal)_2 \cdot 4H_2O$ and $Zn(5\text{-}ClHsal)_2 \cdot 2H_2O$ complexes.

EXPERIMENTAL

Preparation of the complexes

The preparation and analysis data of the $M(5\text{-}XHsal)_2 \cdot 2H_2O$ (M = Cd(II), Mn(II), Zn(II); X = Cl, Br, I, NO_2) and $Ni(5\text{-}XHsal)_2 \cdot 4H_2O$ (X = Cl, Br, I, NO_2) compounds were reported earlier [13,14]. All the elementary analyses (M, C) and IR spectra were in good agreement with the proposed formulae.

TG studies

Thermogravimetric studies were carried out isothermally on a Mettler TG 50 thermobalance in an air flow at a rate of 200 $cm^3\ min^{-1}$. The amount of sample used was between 7 and 12 mg. The kinetic parameters were determined on the basis of the general kinetic relation

$$g(\alpha) = \int_{T_0}^{T_1} k(T)\,dt \qquad (1)$$

where $k(T) = k_0 \exp(-E_a/RT)$ (the Arrhenius law), k_0 = the frequency

TABLE 1

Kinetics function $g(\alpha)$ for heterogeneous solid-state reactions

$g(\alpha)$	Symbol	Rate-controlling process
α^2	D_1	One-dimensional diffusion
$\alpha + (1-\alpha)\ln(1-\alpha)$	D_2	Two-dimensional diffusion
$[1-(1-\alpha)^{1/3}]^2$	D_3	Three-dimensional diffusion (Jander function)
$1-(2/3)\alpha-(1-\alpha)^{2/3}$	D_4	Three-dimensional diffusion (Ginstling–Brounshtein function)
$\ln[\alpha/(1-\alpha)]$	A_u	Autocatalytic reaction (Prout–Tompkins function)
$1-(1-\alpha)^{1/n}$	R_n	Phase-boundary reaction; $n = 1$, 2 and 3 (one-, two- and three-dimensional, respectively)
$[-\ln(1-\alpha)]^{1/m}$	A_m	Random nucleation: $m = 1$ Random nucleation and subsequent growth: $m = 2$, 3 and 4 (Avrami–Erofeev functions)

factor, E_a = the activation energy and α = the mole fraction. For the isothermal analysis the general equation (1) is simply $g(\alpha) = kt$. Values of the correlation coefficient and standard deviation were used as a measure of the linearity for the least squares fitting in various $g(\alpha)$ versus t plots. In this work, we used the principal expressions of $g(\alpha)$ (Table 1) indicated in the literature [16].

DSC runs

Enthalpy measurements between 298 and 873 K were performed with a Mettler DSC-20 differential scanning calorimeter at a heating rate of 5 K min^{-1}. The runs were carried out using a dynamic atmosphere of pure air with a flow rate of 50 cm^3 min^{-1}. The samples varied in weight from 4.5 to 11.6 mg.

RESULTS AND DISCUSSION

The compounds $M(C_{14}H_8O_6X_2) \cdot 2H_2O$ or $Ni(C_{14}H_8O_6X_2) \cdot 4H_2O$ (M = Cd, Mn, Zn; X = Cl, Br, I, NO_2) are stable at a room temperature. They can be heated up to 303–313 K without decomposition. The non-isothermal TG curves for the thermal decomposition of cadmium(II)-bis(2-hydroxy-5-chlorobenzoato)dihydrate, zinc(II)-bis(2-hydroxy-5-bromobenzoato)dihydrate, manganese(II)-bis(2-hydroxy-5-iodobenzoato)dihydrate and cadmium(II)-bis(2-hydroxy-5-nitrobenzoato)dihydrate at a heating rate of 5 K min^{-1} are shown in Fig. 1. Except for the 5-nitrosalicylato complexes, which decompose explosively above 523 K, and Cd(II)-bis(2-hydroxy-5-iodobenzoato)dihydrate, which disappears as CdI_2 above 773 K, decomposition takes place in three stages: dehydration, the loss of one free ligand acid and the loss of the second ligand acid molecule, which further decomposes to the corresponding phenol and carbon dioxide. The final decomposition product is the metal oxide.

In order to calculate the kinetic parameters, the isothermal TG runs were performed at 3–5 different temperatures for each compound. The advantage of this method compared with the non-isothermal method is that the mechanism and the order of the reaction are not assumed, all kinetic parameters being determined from the experimental data.

The interpretation of the dominant rate-controlling factor is very complicated in the decomposition of coordination compounds in the solid state. This rate-controlling factor is known only in the dehydration–anation processes of some octahedral complexes [17,18]. In the present compounds the escape of water molecules from the crystal lattice happens more or less easily. During this stage the loss of other decomposition products is minimal, which makes the kinetic study of this process feasible.

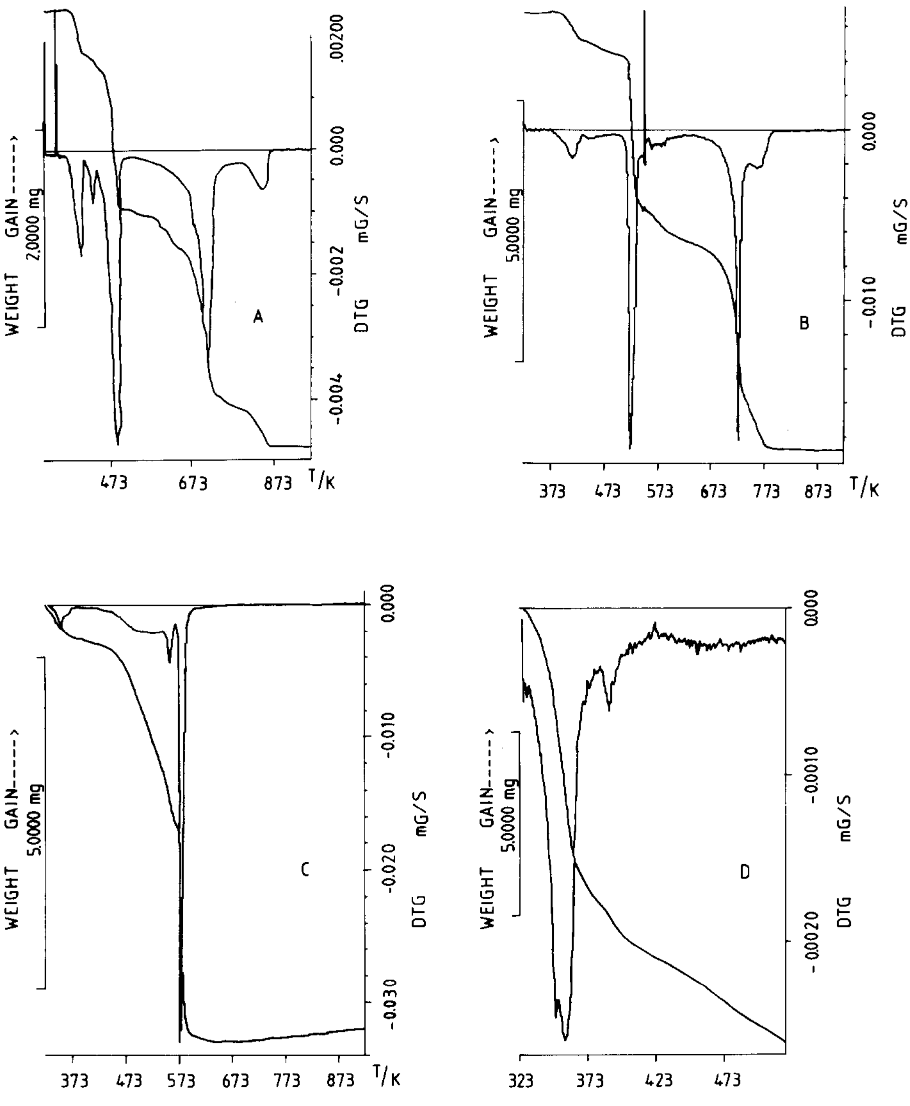

Fig. 1. TG curves of $Cd(5\text{-}ClHsal)_2 \cdot 2H_2O$ (A), $Zn(5\text{-}BrHsal)_2 \cdot 2H_2O$ (B), $Mn(5\text{-}IHsal)_2 \cdot 2H_2O$ (C) and $Cd(5\text{-}NO_2Hsal)_2 \cdot 2H_2O$ (D) heated in air.

Equation (1) was used to describe the dehydration process of the studied compounds by plotting $g(\alpha)$ against t, and the appropriate plot should give a straight line with a slope of k. On the basis of the values of the regression coefficient and standard deviation, a phase-boundary reaction mechanism, R_n, proved to be the best model.

Figure 2 shows the temperature dependence of α for the 5-substituted nickel(II)salicylato tetrahydrate complexes. These plots, α against mole-fraction decomposed, reveal that for 5-substituted nickel compounds the ther-

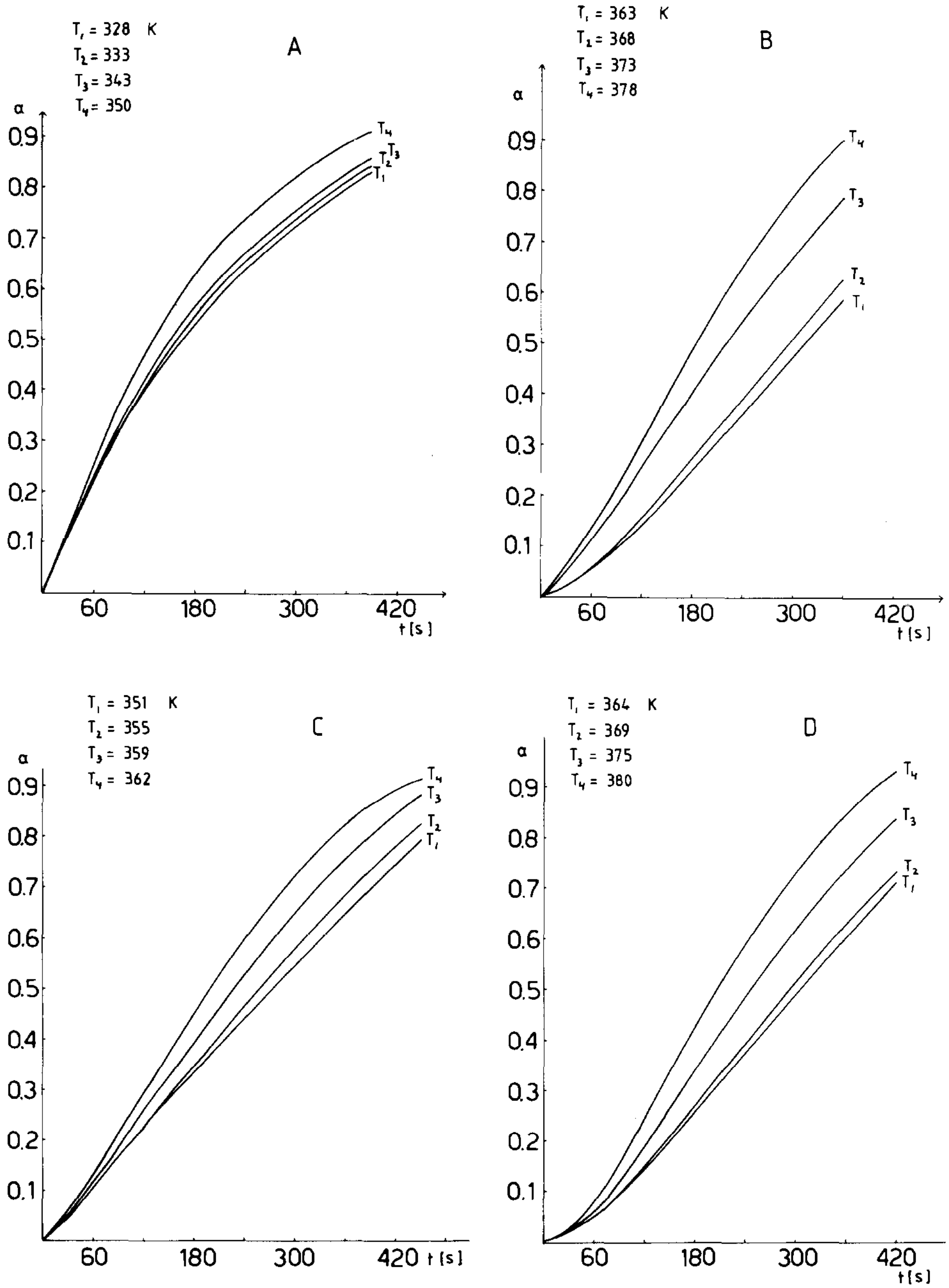

Fig. 2. Effect of temperature on the isothermal dehydration of 5-substituted nickel(II)-salicylato tetrahydrate compounds. The plots show the fractional decomposition of Ni(5-ClHsal)$_2$·4H$_2$O (A), Ni(5-BrHsal)$_2$·4H$_2$O (B), Ni(5-IHsal)$_2$·4H$_2$O (C) and Ni(5-NO$_2$-Hsal)$_2$·4H$_2$O (D).

mal stability obeys the order Cl < I < Br ≈ NO_2. Also, the thermal stability order Br < I < Cl < NO_2 for 5-substituted manganese(II) salicylato compounds deviate from the expective order NO_2 < I < Br < Cl found both for the studied cadmium and zinc complexes, where thermal stability decreases with increasing ion size of the substituent. The reason for this may be the different coordination of the M^{2+} ion. For the unsubstituted salicylato complexes the crystal structures have been solved [6,12]. The Cd, Mn, Ni and Zn complexes crystallize monoclinically and Mn and Ni belong to the space group $P2_1/c$, Cd to the space group $P2_1/a$ and Zn to group $C2$. Mn^{2+} and Ni^{2+} ions have extremely distorted octahedral and octahedral coordinations respectively, while Zn^{2+} and Cd^{2+} have tetrahedral coordinations.

The α curves of $Ni(5\text{-}NO_2Hsal)_2 \cdot 4H_2O$ (Fig. 2), as well as those for $Mn(5\text{-}NO_2Hsal)_2 \cdot 2H_2O$ (Fig. 3), have a pronounced sigmoid shape. This should, according to Brown et al. [19], mean that the physical model will correspond to the nucleation–growth model. Our calculations show that the best model to describe dehydration of the studied complexes is a phase boundary reaction model, R_n, but a nucleation–growth mechanism, A_m, is close to it. In Tables 2–5 are given values of the rate constant, k, at different temperatures for the dehydration process of the studied complexes. Figure 4 shows that temperature dependence of k for the halogen substituted

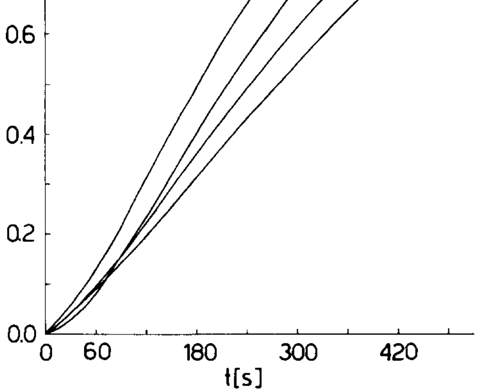

Fig. 3. Plots of α versus t at different temperatures for the isothermal dehydration of $Mn(5\text{-}NO_2Hsal)_2 \cdot 2H_2O$.

TABLE 2

The rate constant, k, for the isothermal dehydration of the 5-substituted cadmium(II)salicylato complexes in terms of R_n and A_m functions

Compound	T (K)	k ($\times 10^4$ s^{-1})	
		R_n	A_m
		$n = 1.0$	$m = 1.8$
$Cd(5\text{-}ClHsal)_2 \cdot 2H_2O$	373	8.65	12.6
	378	11.3	15.3
	383	14.6	19.2
	388	18.8	24.9
	393	24.0	35.8
		$n = 1.0$	$m = 2.4$
$Cd(5\text{-}BrHsal)_2 \cdot 2H_2O$	393	22.0	27.4
	398	29.9	35.2
	403	41.1	54.0
		$n = 2.0$	$m = 1.4$
$Cd(5\text{-}IHsal)_2 \cdot 2H_2O$	388	12.9	29.5
	393	16.1	37.6
	398	21.7	55.7
		$n = 3.2$	$m = 1.0$
$Cd(5\text{-}NO_2Hsal)_2 \cdot 2H_2O$	343	5.65	20.3
	349	9.85	39.6
	352	12.3	53.9
	353	13.2	59.7
	355	15.0	73.5

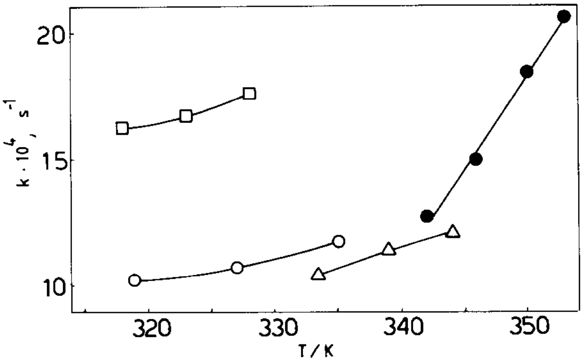

Fig. 4. Rate constant k against temperature for dehydration of 5-substituted manganese(II)-salicylato complexes calculated according to phase boundary reaction model. Symbols △, ○, □ and ● refer to $Mn(5\text{-}ClHsal)_2 \cdot 2H_2O$, $Mn(5\text{-}BrHsal)_2 \cdot 2H_2O$, $Mn(5\text{-}IHsal)_2 \cdot 2H_2O$ and $Mn(5\text{-}NO_2Hsal)_2 \cdot 2H_2O$ compounds, respectively.

TABLE 3

The rate constant, k, for the isothermal dehydration of the 5-substituted manganese(II)salicylato complexes in terms of R_n and A_m functions

Compound	T (K)	k ($\times 10^4$ s^{-1})	
		R_n	A_m
		$n = 3.2$	$m = 1.4$
$Mn(5\text{-}ClHsal)_2 \cdot 2H_2O$	334	10.4	33.1
	339	11.4	36.6
	344	12.1	39.2
		$n = 3.2$	$m = 1.4$
$Mn(5\text{-}BrHsal)_2 \cdot 2H_2O$	319	10.2	32.7
	327	10.7	34.7
	335	11.7	38.4
		$n = 1.2$	$m = 2.4$
$Mn(5\text{-}IHsal)_2 \cdot 2H_2O$	318	16.2	18.9
	323	16.7	19.4
	328	17.6	20.8
		$n = 2.0$	$m = 2.0$
$Mn(5\text{-}NO_2Hsal)_2 \cdot 2H_2O$	342	12.7	22.7
	346	14.9	25.9
	350	18.4	32.0
	353	20.6	36.0

manganese complexes is very small. It can be also seen in this plot, and, especially, in Fig. 5, that the dependence of k on temperature is linear only around the peak under a narrow temperature range. The peak temperatures for the dehydration of $Ni(5\text{-}ClHsal)_2 \cdot 4H_2O$ and $Ni(5\text{-}BrHsal)_2 \cdot 4H_2O$ are 358 and 383 K, respectively.

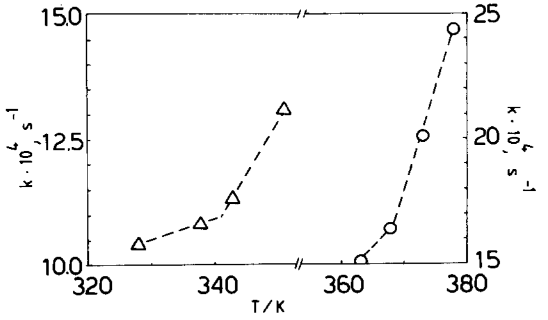

Fig. 5. Rate constant k versus T for isothermal dehydration of powdered nickel(II)-bis(2-hydroxy-5-chlorobenzoato)tetrahydrate (△) and nickel(II)-bis(2-hydroxy-5-bromobenzoato)tetrahydrate (○).

TABLE 4

The rate constant, k, for the isothermal dehydration of the 5-substituted nickel(II)salicylato complexes in terms of R_n and A_m functions

Compound	T (K)	k ($\times 10^4$ s^{-1})	
		R_n	A_m
		$n = 3.2$	$m = 1.2$
Ni(5-ClHsal)$_2$·4H$_2$O	328	10.4	38.4
	338	10.8	39.9
	343	11.3	41.9
	351	13.1	50.7
		$n = 1.4$	$m = 2.2$
Ni(5-BrHsal)$_2$·4H$_2$O	363	15.1	21.3
	368	16.4	22.6
	373	20.1	26.6
	378	24.4	34.2
		$n = 1.6$	$m = 2.2$
Ni(5-IHsal)$_2$·4H$_2$O	351	14.3	20.7
	355	15.5	22.4
	359	17.4	25.3
	362	18.5	27.3
		$n = 1.4$	$m = 2.0$
Ni(5-NO$_2$Hsal)$_2$·4H$_2$O	369	16.5	24.6
	375	19.6	29.2
	380	22.7	35.8

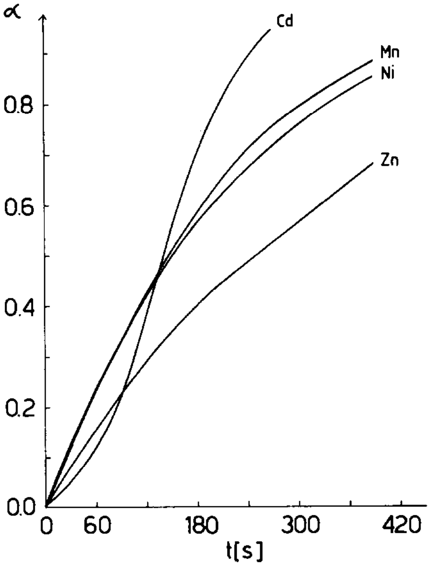

Fig. 6. Plots of α versus t for the dehydration of 5-chlorosubstituted metal(II) salicylato compounds. Temperatures for cadmium, manganese, nickel and zinc complexes are 403, 344, 343 and 403 K, respectively.

TABLE 5

The rate constant, k, for the isothermal dehydration of the 5-substituted zinc(II)salicylato complexes in terms of R_n and A_m functions

Compound	T (K)	k ($\times 10^4$ s^{-1})	
		R_n	A_m
		$n = 1.8$	$m = 2.4$
$Zn(5\text{-}ClHsal)_2 \cdot 2H_2O$	403	10.6	14.4
	412	17.3	23.4
	416	19.9	27.3
		$n = 2.0$	$m = 1.6$
$Zn(5\text{-}BrHsal)_2 \cdot 2H_2O$	403	12.9	28.3
	408	17.0	36.3
	412	20.0	43.8
		$n = 2.8$	$m = 1.4$
$Zn(5\text{-}IHsal)_2 \cdot 2H_2O$	398	10.9	31.7
	403	12.0	34.7
	411	15.6	45.2
	415	21.3	63.8
		$n = 1.6$	$m = 1.8$
$Zn(5\text{-}NO_2Hsal)_2 \cdot 2H_2O$	338	15.4	26.7
	343	17.0	29.9
	348	18.5	33.2

The dependence of thermal stability on the metal ion, M^{2+}, is shown in Fig. 6 for 5-chlorosubstituted metal salicylato complexes. Taking into account dehydration temperatures, the thermal stability of the studied compounds obeys the order Zn > Cd > Ni > Mn. The same stability order has also been found for 5-bromo and 5-iodo complexes, while for 5-nitro compounds the order is Ni > Mn > Zn > Cd.

The values of the kinetic parameters listed in Table 6 have been determined using both the phase boundary, R_n and nucleation–growth-controlled, A_m, models. The mean values of the activation energies for the dehydration process are 85, 65, 44 and 44 kJ mol^{-1} for cadmium, zinc, nickel and manganese compounds, respectively. Table 6 shows that the E_a values are nearly independent of the nature of the substituent for a given central atom. Activation energy values for the dehydration process nearly coincide with those reported for unsubstituted metalsalicylato compounds, excluding the substituted cadmium(II) compounds for which E_a values are significantly greater than those for the unsubstituted compound [15].

Table 7 and Fig. 7 show ΔH values for the thermal decomposition of 5-chlorosubstituted Mn, Ni and Zn compounds between 298 and 873 K. Again, as in the case of the unsubstituted compounds, the first two stages are endothermic and the third step is strongly exothermic [15]. Also, the

TABLE 6

Kinetic parameters derived from the Arrhenius plot by means of isothermal TG

Compound	g(α)	E (kJ mol^{-1})	ln k_0 (s^{-1})	$-r$
Cd(5-ClHsal)$_2$·2H$_2$O	$A_{1.8}$	62.7 ± 5.0	13.47 ± 1.58	0.9905
	$R_{1.0}$	62.2 ± 0.1	13.00 ± 0.02	1.0000
Cd(5-BrHsal)$_2$·2H$_2$O	$A_{2.4}$	89.2 ± 18.4	21.33 ± 5.55	0.9889
	$R_{1.0}$	82.4 ± 1.2	19.08 ± 0.37	0.9996
Cd(5-IHsal)$_2$·2H$_2$O	$A_{1.4}$	81.4 ± 12.2	19.37 ± 3.75	0.9899
	$R_{2.0}$	66.9 ± 6.2	14.07 ± 1.91	0.9972
Cd(5-NO$_2$Hsal)$_2$·2H$_2$O	$A_{1.0}$	108.5 ± 0.7	31.82 ± 0.25	0.9999
	$R_{3.2}$	83.0 ± 3.3	21.64 ± 1.13	0.9976
Mn(5-NO$_2$Hsal)$_2$·2H$_2$O	$A_{2.0}$	43.4 ± 3.1	9.15 ± 1.06	0.9985
	$R_{2.0}$	45.3 ± 2.4	9.25 ± 0.85	0.9995
Ni(5-BrHsal)$_2$·4H$_2$O	$A_{2.2}$	47.9 ± 7.3	9.54 ± 2.21	0.9915
	$R_{1.4}$	46.0 ± 0.3	8.61 ± 0.10	0.9999
Ni(5-NO$_2$Hsal)$_2$·4H$_2$O	$A_{2.0}$	38.5 ± 4.1	6.52 ± 1.31	0.9955
	$R_{1.4}$	32.7 ± 1.5	4.24 ± 0.47	1.0000
Zn(5-ClHsal)$_2$·2H$_2$O	$A_{2.4}$	70.9 ± 5.1	14.62 ± 1.50	1.0002
	$R_{1.8}$	70.3 ± 5.0	14.14 ± 1.48	0.9986
Zn(5-BrHsal)$_2$·2H$_2$O	$A_{1.6}$	69.2 ± 3.5	14.78 ± 1.04	1.0001
	$R_{2.0}$	69.3 ± 11.0	14.00 ± 3.24	0.9981
Zn(5-IHsal)$_2$·2H$_2$O	$A_{1.4}$	53.8 ± 11.5	10.45 ± 3.40	0.9577
	$R_{2.8}$	52.0 ± 9.8	8.83 ± 2.90	0.9660

peak temperatures determined by DSC agree with the thermal stability order mentioned above for halogen substituted compounds. It seems that the dehydration enthalpy values are about 25–30 kJ mol^{-1} lower for substituted

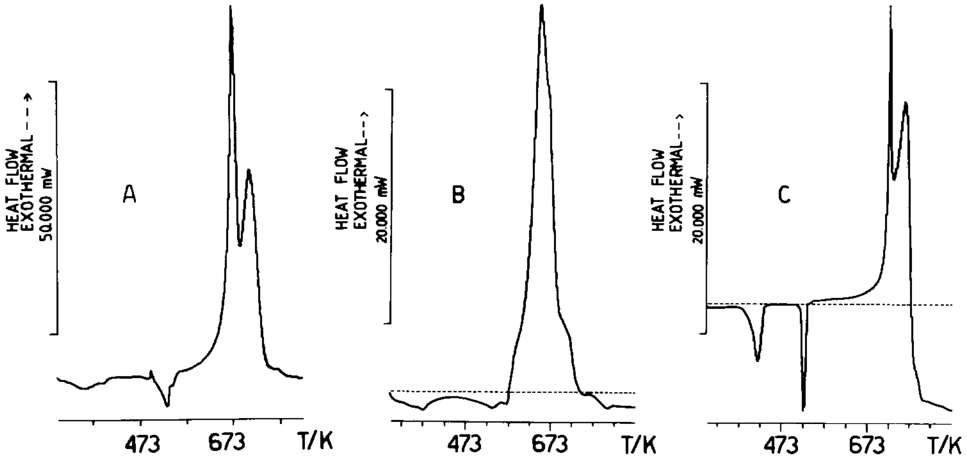

Fig. 7. DSC curves for the Mn(5-ClHsal)$_2$·2H$_2$O (A), Ni(5-ClHsal)$_2$·4H$_2$O (B) and Zn(5-ClHsal)$_2$·2H$_2$O (C).

TABLE 7

DSC data on decomposition of 5-chlorometal salicylato compounds studied

	Stage I			Stage II			Stage III		
	Temperature range (K)	T_P (K)	ΔH (kJ mol^{-1})	Temperature range (K)	T_P (K)	ΔH (kJ mol^{-1})	Temperature range (K)	T_P (K)	ΔH (kJ mol^{-1})
Mn(5-ClHsal)$_2$·2H$_2$O	303–421	351	87	493–558	528	83	584–777	677	−1816
Ni(5-ClHsal)$_2$·4H$_2$O	303–441	378	84	456–559	529	51	566–810	670	−2920
Zn(5-ClHsal)$_2$·2H$_2$O	369–437	414	114	502–544	524	105	623–850	727	−1696

than unsubstituted Mn and Ni compounds. For zinc compounds there seems to be no difference between 5-substituted or unsubstituted hydration energies. However, the E_a values are, in all cases, lower than the corresponding enthalpy values. The enthalpies for the second decomposition stage are of the same magnitude as for the corresponding unsubstituted compounds. The peak temperatures in Table 7 show that this decomposition stage occurs exactly at the same temperature for all 5-chlorosubstituted compounds studied. The enthalpy values related to the loss of substituted phenol and CO_2 molecules in the third decomposition stage show that the total heat effect introduced from the reaction in this stage is not so exothermic as in the case of the unsubstituted compounds: this means that the presence of substituent in the complex produces an endothermic effect which decreases the total exothermic effect.

CONCLUSION

The thermal dehydration of the studied metal salicylato compounds seems to best follow a phase-boundary reaction model. The thermal stability decreases with increasing substituent size in the case of cadmium and zinc salicylato complexes, but not in the case of manganese and nickel compounds. The possible reason for this is different coordination of the M^{2+} ion. On the other hand, it seems that, for halogen substituents, varying the metal ion for an individual substituent, the thermal stability increases in the order Zn > Cd > Ni > Mn. The same effect for the nitro substituent is, almost, the opposite: Ni > Mn > Zn > Cd.

Activation energies calculated from the Arrhenius law for the dehydration process are lower than the respective enthalpy values. This means that the loss of water molecules take place easily, but there is a rearrangement of α for a complex structure which needs energy. Enthalpy values determined by DSC agree well with those reported for unsubstituted metalsalicylato complexes. It seems that the presence of the substituent in the complex decreases the total exothermic effect of the third decomposition stage of the studied metalsalicylato compounds.

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