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SOLID STATE DECOMPOSITION STUDIES ON METAL SALICYLATES. KINETICS OF ISOTHERMAL DEHYDRATION OF SOME TRANSITION METAL SALICYLATO COMPLEXES

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ABSTRACT

The dehydration of cadmium(II), copper(II), manganese(II), nickel(II) and zinc(II) salicylato complexes were investigated by means of isothermal TG measurements. The Cd, Mn and Zn complexes were dihydrates, Ni complex was a tetrahydrate while Cu formed both dihydrate and tetrahydrate complexes. Thermal decomposition of the studied complexes synthesized using a pure salicylic acid as a ligand occurs in three stages, the oxides finally being formed. The first step being associated to the dehydration of the complexes obeys a phase boundary reaction mechanism. The ΔH values for hydration of Cd, Cu, Mn and Zn dihydrate complexes are 116.5, 76.0, 86.8, 113.3 kJ mol^{-1} and for Cu and Ni tetrahydrates 117.1 and 108.9 kJ mol^{-1}, respectively.

INTRODUCTION

We have previously prepared and characterized by elemental analysis, X-ray measurements, thermal analysis and IR spectra cadmium(II), copper(II), manganese(II), nickel(II) and zinc(II) salicylato hydrates (refs. 1-3). As a continuation of this research we studied kinetics of isothermal dehydration as well as measured ΔH values by DSC for each of three decomposition stages of these complexes.

EXPERIMENTAL

The preparation and analysis data for the studied complexes have been reported earlier (refs. 1-3). Thermogravimetric studies were carried out isothermally on a Mettler TG 50 thermobalance in a flow of air at a rate of 200 ml min^{-1} with samples of 8-12 mg. DSC plots were obtained with a Mettler DSC-20 differential scanning calorimeter at a heating rate of 5 K min^{-1} with 4-7 mg samples in dynamic air atmosphere (50 ml min^{-1}).

The kinetic parameters were determined on the basis of the kinetic relation

$$d\alpha/dt \;=\; k(T)\; f(\alpha) \qquad (1)$$

where $k(T) = k_o \exp(-E_a/RT)$ (Arrhenius law); k_o = frequency factor; E_a = activation energy and α = decomposed fraction. Integrating eqn. (1) and replacing $d\alpha/f(\alpha)$ by the function $g(\alpha)$, which is shown for various mechanisms

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in Table 1, the equation for the TG curve can be obtained

$$\int_{o}^{1} g(\alpha) = \int_{T_o}^{T_1} k(T)\, dt \qquad (2)$$

For isothermal analysis the general equation (2) is simply $g(\alpha) = kt$. Correlation coefficients, r, and standard deviations, s, were used as a measure of the linearity for the least squares fitting in various $g(\alpha)$ vs. t plots.

TABLE 1

Kinetic functions $g(\alpha)$ of heterogenous 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-Broushtein 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-Erofeyev functions)

RESULTS AND DISCUSSION

Table 2 shows the correlation coefficients, r, and standard deviations, s, in the least square fitting of $g(\alpha)$ against t plots using isothermal TG data. On the basis of the values of r and s, R_n is the best model but A_m is very close to it. Figure 1 shows plots of α vs. t. The results show that the thermal dehydration of the complexes obeys the temperature order Cu < Zn < Ni ≈ Cd < Mn. Table 3 lists the values of k at various temperatures, obtained from the plots using the mean values of n and m over the studied temperature range for each complex. The kinetic parameters E_a and $\ln k_o$ are given in Table 4. It is seen that nearly identical activation energy and frequency factor result from either the A_m or R_n mechanism. Table 5 and Fig. 2 show ΔH values for the thermal decomposition of the studied metal salicylato complexes. There is three stages in decomposition of these complexes in order: dehydration, the release of first salicylato ligand and the release of the other salicylato ligand combined with the formation of metal oxide. The first two stages seems to be endothermic while third step is strongly exothermic. The peak temperatures (Table 5) of dehydration stage agree with

TABLE 2

The correlation coefficient r and standard deviation s for the least square fitting of g(α) vs. t plot for the isothermal dehydration of some metal salicylato complexes in the α range 0.1 - 0.9.

Compound	T(K)	Coef-ficient	g(α)											
			D_1	D_2	D_3	D_4	A_u	A_1	A_2	A_3	A_4	R_1	R_2	R_3
$Cd(Hsal)_2\cdot 2H_2O$	388.15	r	0.9683	0.9594	0.9487	0.9738	0.9781	0.9937	0.9983	0.9927	0.9882	0.9995	0.9977	0.9966
		$s\cdot 10^2$	2.3	1.6	0.5	1.6	22	2.6	1.3	2.3	2.4	0.5	0.7	0.6
$Cu(Hsal)_2.2H_2O$	328.15	r	0.9913	0.9814	0.9618	0.9051	0.9804	0.9939	0.9972	0.9893	0.9832	0.9936	0.9995	0.9990
		$s\cdot 10^2$	3.2	3.5	1.8	2.9	25	6.1	2.6	3.7	3.7	2.9	0.6	0.6
$Mn(Hsal)_2\cdot 2H_2O$	402.15	r	0.9988	0.9925	0.9773	0.9100	0.9896	0.9970	0.9969	0.9917	0.9881	0.9914	0.9994	0.9998
		$s\cdot 10^2$	1.0	2.0	1.25	1.73	13	3.7	2.1	2.5	2.3	2.7	0.5	0.2
$Ni(Hsal)_2\cdot 4H_2O$	373.15	r	0.9938	0.9833	0.9639	0.9425	0.9964	0.9913	0.9994	0.9978	0.9960	0.9981	0.9994	0.9978
		$s\cdot 10^2$	2.2	2.8	1.4	1.4	7.5	5.9	0.8	1.2	1.3	1.2	0.5	0.7
$Zn(Hsal)_2\cdot 2H_2O$	357.15	r	0.9642	0.9491	0.9292	0.9449	0.9515	0.9882	0.9958	0.9844	0.9749	0.9999	0.9967	0.9942
		$s\cdot 10^2$	3.7	2.9	1.0	2.6	40	5.0	2.5	3.9	4.2	0.3	1.0	0.9

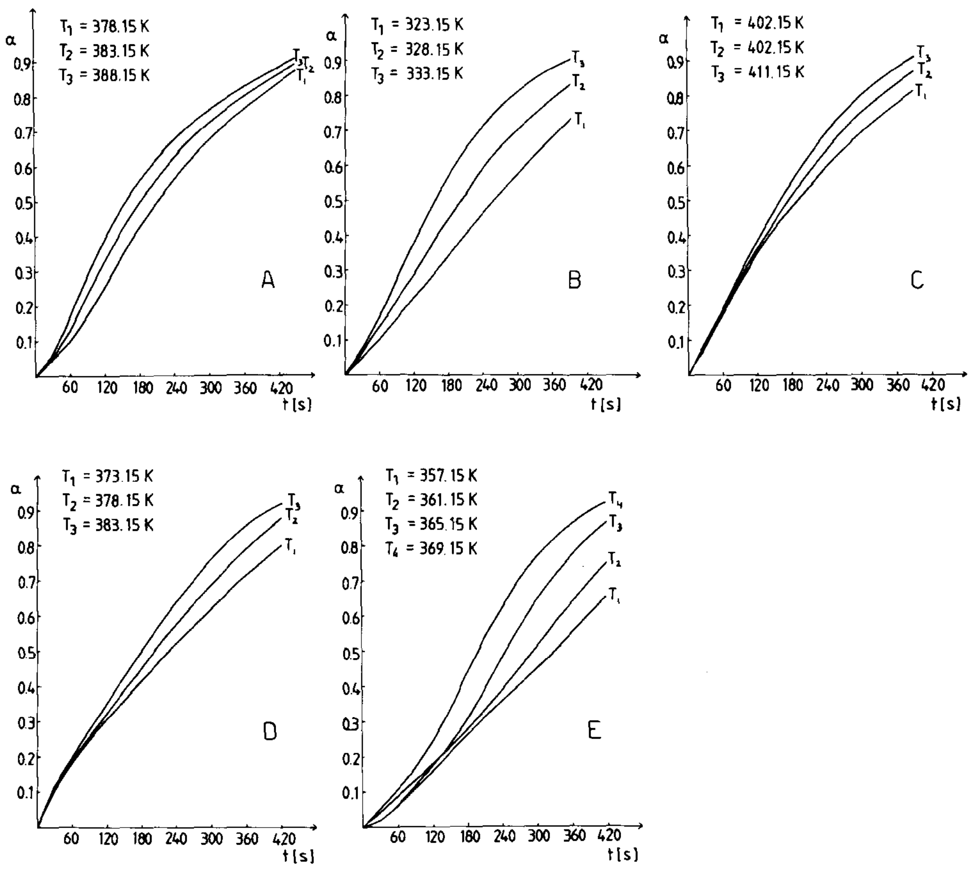

Fig. 1. Plot of α vs. t at different temperatures for the $Cd(Hsal)_2 \cdot 2H_2O$, A; $Cu(Hsal)_2 \cdot 2H_2O$, B; $Mn(Hsal)_2 \cdot 2H_2O$, C; $Ni(Hsal)_2 \cdot 4H_2O$, D and $Zn(Hsal)_2 \cdot 2H_2O$, E.

TABLE 3

The rate constants, k, for the isothermal dehydration of the metal salicylato complexes in terms of R_n and A_m functions.

Compound	T(K)	$k \cdot 10^4$, s^{-1}	
		R_n	A_m
		n = 1.6	n = 1.6
$Cd(Hsal)_2 \cdot 2H_2O$	383.15	18.31	36.19
	393.15	23.11	44.18
	403.15	31.30	59.14
	413.15	36.93	72.68
		n = 2.8	n = 1.4
$Cu(Hsal)_2 \cdot 2H_2O$	323.15	9.98	30.13
	328.15	12.65	37.73
	333.15	15.52	46.91
		n = 2.6	n = 1.6
$Mn(Hsal)_2 \cdot 2H_2O$	402.15	12.09	30.10
	407.15	14.17	35.34
	411.15	15.99	40.21
		n = 2.0	n = 2.2
$Ni(Hsal)_2 \cdot 2H_2O$	373.15	12.56	20.39
	378.15	15.23	24.48
	383.86	17.52	28.24
		n = 1.8	n = 2.0
$Zn(Hsal)_2 \cdot 2H_2O$	357.15	11.56	19.85
	361.15	14.53	24.31
	365.15	19.81	33.11
	369.15	21.08	35.76

TABLE 4

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

Compound	g(α)	E, kJ mol^{-1}	ln A, s^{-1}	−r
$Cd(Hsal)_2 \cdot 2H_2O$	$A_{1.6}$	31.4 ± 1.8	4.20 ± 0.54	0.9968
	$R_{1.6}$	31.7 ± 2.1	3.05 ± 0.68	0.9955
$Cu(Hsal)_2 \cdot 2H_2O$	$A_{1.4}$	39.5 ± 0.1	8.91 ± 0.08	1.0000
	$R_{2.8}$	39.4 ± 1.4	7.77 ± 0.50	0.9997
$Mn(Hsal)_2 \cdot 2H_2O$	$A_{1.6}$	44.1 ± 9.6	7.40 ± 2.83	0.9998
	$R_{2.6}$	42.8 ± 14.3	6.11 ± 4.23	1.0012
$Ni(Hsal)_2 \cdot 4H_2O$	$A_{2.2}$	36.1 ± 3.7	5.45 ± 1.19	0.9963
	$R_{2.0}$	36.9 ± 5.4	5.23 ± 1.72	0.9934
$Zn(Hsal)_2 \cdot 2H_2O$	$A_{2.0}$	56.8 ± 8.3	12.91 ± 2.74	0.9804
	$R_{1.8}$	57.8 ± 9.3	12.74 ± 3.08	0.9748

TABLE 5

DSC data on decomposition of studied metal salicylato complexes.

Compound	Stage I			Stage II			Stage III		
	T_{range}(K)	T_p(K)	ΔH (kJ mol^{-1})	T_{range}(K)	T_p(K)	ΔH (kJ mol^{-1})	T_{range}(K)	T_p(K)	ΔH (kJ mol^{-1})
$Cd(Hsal)_2 \cdot 2H_2O$	363–447	407	116.5	447–494	463	51.47	625–703	691	-1991
$Cu(Hsal)_2 \cdot 2H_2O$	332–382	352	75.96	–	–	–	541–619	606	-3389
$Cu(Hsal)_2 \cdot 4H_2O$	298–421	353	117.1	–	–	–	541–616	604	-3656
$Mn(Hsal)_2 \cdot 2H_2O$	298–438	423	86.77	–	–	–	555–643	612	-2511
$Ni(Hsal)_2 \cdot 4H_2O$	298–448	404	108.9	–	–	–	558–654	642	-3507
$Zn(Hsal)_2 \cdot 2H_2O$	348–391	372	113.3	498–532	520	88.65	672–738	733	-1036

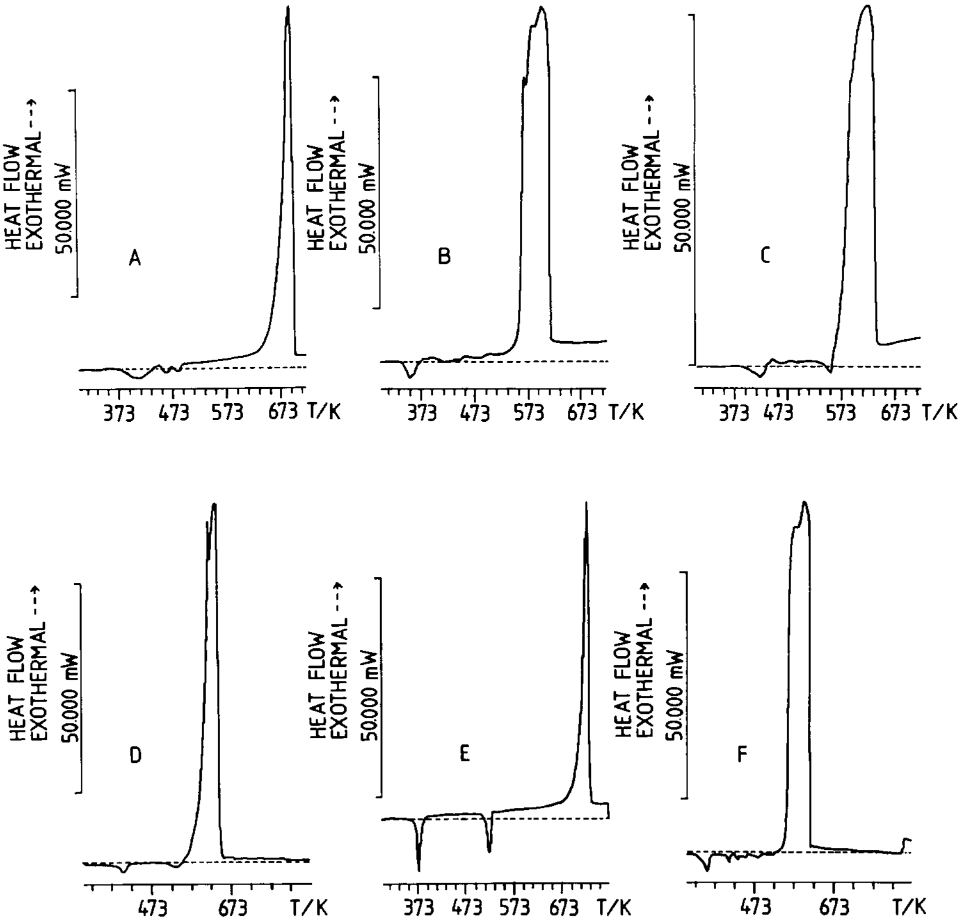

Fig. 2. DSC curves for the Cd(Hsal)$_2$·2H$_2$O, A; Cu(Hsal)$_2$·2H$_2$O, B; Mn(Hsal)$_2$·2H$_2$O, C; Ni(Hsal)$_2$·4H$_2$O, D; Zn(Hsal)$_2$·2H$_2$O, E and Cu(Hsal)$_2$·4H$_2$O, F.

temperature order derived from isothermal TG data and mentioned above. The dehydration temperature seems increase with increasing ionic radius. The peak temperatures for the third step obeys the order Cu < Mn < Ni < Cd < Zn.

The activation energy of the dehydration process is very low (ca. 40 kJ mol^{-1}) and considerably smaller than the ΔH value. This means that the loss of water molecules take place easily but there is a great rearrangement in structure which needs energy.

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