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SOLID-STATE DECOMPOSITION STUDIES ON 5-SUBSTITUTED SALICYLATES. KINETICS OF THE ISOTHERMAL DECOMPOSITION OF HYDRATED COPPER(II) 5-SUBSTITUTED SALICYLATES

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ABSTRACT

The kinetics and thermodynamics of the thermal decomposition of powdered copper(II)–bis(2-hydroxy-5-chlorobenzoato)trihydrate, copper(II)–bis(2-hydroxy-5-bromobenzoato)trihydrate or copper(II)–bis(2-hydroxy-5-iodobenzoato)trihydrate to the corresponding monohydrates and copper(II)–bis(2-hydroxy-5-nitrobenzoato)dihydrate to the anhydrous complex were studied by means of TG and DSC at constant temperatures. The thermal decomposition process, involving the loss of two water molecules, follows a phase boundary reaction mechanism. The activation energies for the copper(II)–bis(2-hydroxy-5-chlorobenzoato)trihydrate, copper(II)–bis(2-hydroxy-5-bromobenzoato)trihydrate, copper(II)–bis(2-hydroxy-5-iodobenzoato)trihydrate and copper(II)–bis(2-hydroxy-5-nitrobenzoato)dihydrate are 132.9, 134.8, 141.5 and 127.4 kJ mol^{-1}, respectively. The enthalpy changes are all endothermic and nearly equal to the corresponding activation energies.

INTRODUCTION

Recently, we studied the composition and stability of complexes formed in aqueous sodium perchlorate solutions of copper(II) ions and 5-substituted salicylic acids as well as the partition of copper(II) between the aqueous and organic phase in the presence of 5-chloro-, 5-bromo-, 5-iodo- or 5-nitro-salicylic acids [1,2]. In earlier studies concerning the thermal decomposition of copper(II)–bis(2-hydroxy-5-chlorobenzoato)trihydrate (**I**), copper(II)–bis(2-hydroxy-5-bromobenzoato)trihydrate (**II**) and copper(II)–bis(2-hydroxy-5-iodobenzoato)trihydrate (**III**), we noted that the thermal dehydration of these complexes takes place in two stages [3].

The present paper forms a part of the series on the thermal behaviour and kinetics of 5-substituted metal salicylato complexes.

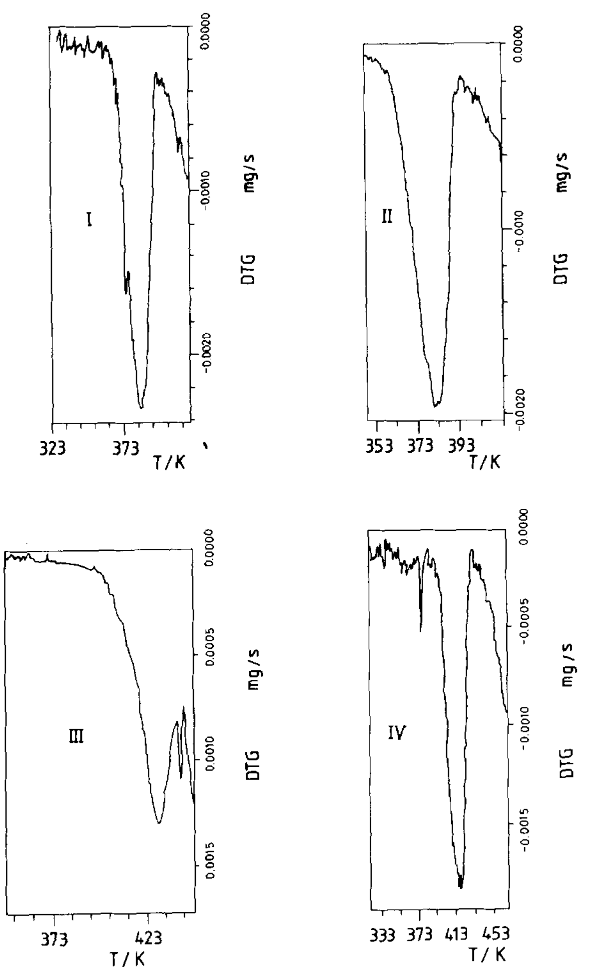


Fig. 1. DTG plots of $Cu(5\text{-}ClHL)_2 \cdot 3\ H_2O$ (**I**); $Cu(5\text{-}BrHL)_2 \cdot 3\ H_2O$ (**II**); $Cu(5\text{-}IHL)_2 \cdot 3\ H_2O$ (**III**); and $Cu(5\text{-}NO_2HL)_2 \cdot 2\ H_2O$ (**IV**).

EXPERIMENTAL

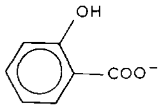
The preparation and analysis of the present copper(II) complexes have been presented earlier [3]. The TG, DTG and DSC measurement of the compounds were carried out in air on a Mettler TA 3000 thermal analysis system. The sample weights varied between 5 and 7 mg. A heating rate of 5 K min^{-1} was used in each run. The calibration of temperature and enthalpy change for the thermal analysis system were the same as those given in ref. 3.

RESULTS AND DISCUSSION

Figure 1 shows DTG curves for the dehydration reaction

$$Cu(5\text{-}XHL)_2 \cdot nH_2O \rightarrow Cu(5\text{-}XHL)_2 \cdot (n\text{-}2)\ H_2O + 2\ H_2O \qquad (1)$$

where X = Cl (**I**), Br (**II**), I (**II**) or NO_2 (**IV**) and HL =



Chemical analyses of these complexes showed that $n = 3$ when X = Cl, Br or I and $n = 2$ when X = NO_2, respectively.

The loss of the water molecules from $Cu(5\text{-}IHL)_2 \cdot 3\ H_2O$ or $Cu(5\text{-}NO_2HL) \cdot 2\ H_2O$ complexes begins at higher temperatures than in the case of 5-chloro- or 5-bromocomplexes (Fig. 1). We have previously stated that the decomposition of compounds **I**, **II** and **III** occurs in three stages. Step I corresponds to the simultaneous loss of two H_2O molecules. In the next step the loss of one H_2O molecule and the loss of ligand acid partly coincide. In the third step the volatile products are substituted phenols and carbon dioxide and the final product is CuO. According to the mass spectra of the decomposition products, all other decomposition reactions except reaction (1) partly coincide and, therefore, it is only possible to study the kinetics of the first decomposition stage.

For the isothermal dehydration reactions of hydrated copper(II)–5-chloro-, copper(II)–5-bromo-, copper(II)–5-iodo- and copper(II)–5-nitrosalicylates, the following equation is assumed

$$F(\alpha) = kt \qquad (2)$$

where $F(\alpha)$ is a function depending on the isothermal dehydration mechanism, α is the fraction dehydrated at time, t, and k is the rate constant. Table 1 lists the kinetic functions commonly used for the solid decomposition [4,5]. The $F(\alpha)$ pertinent to the decomposition can be found by plotting it against t; the appropriate value should give a straight line with slope k. The correlation coefficient r and the error δ as a measure of the linearity are

TABLE 1

Various mechanistic functions $F(\alpha)$ used in the isothermal decomposition of solids

Symbol	$F(\alpha)$
D_1	α^2
D_2	$\alpha + (1-\alpha)\ln(1-\alpha)$
D_3	$[1-(1-\alpha)^{1/3}]^2$
D_4	$1-2\alpha/3-(1-\alpha)^{2/3}$
A_u	$\ln[\alpha/(1-\alpha)]$
A_m	$[-\ln(1-\alpha)]^{1/m}$; $m = 1, 2, 3, 4$
R_n	$1-(1-\alpha)^{1/n}$; $n = 1, 2, 3$

TABLE 2

Coefficients as a measure of linearity for the least squares fitting in the F(α) vs. t plot at given temperatures in the α range 0.1–0.95

Complex	T (K)	Coefficient[a]	F(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
I	383.15	r	0.9949	0.9997	0.9916	0.9130	0.9995	0.9956	0.9997	0.9994	0.9989	0.9852	0.9989	0.9998
		$\delta * 10^2$	2.1	0.5	1.4	0.4	2.9	6.5	0.6	0.6	0.6	2.5	0.7	0.3
II	373.15	r	0.9942	0.9996	0.9875	0.878	0.9994	0.9947	0.9997	0.9982	0.9969	0.9785	0.9982	0.9999
		$\delta * 10^2$	2.6	0.7	1.8	0.9	3.6	7.8	0.8	1.2	1.2	3.7	1.1	0.1
III	418.15	r	0.9995	0.9996	0.9965	0.9677	0.9989	0.9996	0.9993	0.9984	0.9978	0.9953	0.9993	0.9998
		$\delta * 10^2$	0.4	0.3	0.3	0.3	2.1	0.8	0.5	0.5	0.5	1.0	0.3	0.1
IV	411.15	r	0.9967	0.9996	0.9906	0.9013	0.9985	0.9978	0.9990	0.9968	0.9952	0.9834	0.9980	0.9997
		$\delta * 10^2$	1.8	0.6	1.2	0.8	4.7	4.1	1.2	1.4	1.3	3.2	1.0	0.3

[a] r is the so-called correlation coefficient and δ is the error defined by the equation $\delta = [\Sigma\epsilon_i^2/(N-1)]^{1/2}$, where ϵ_i is the deviation from the straight line and N is the number of experimental data.

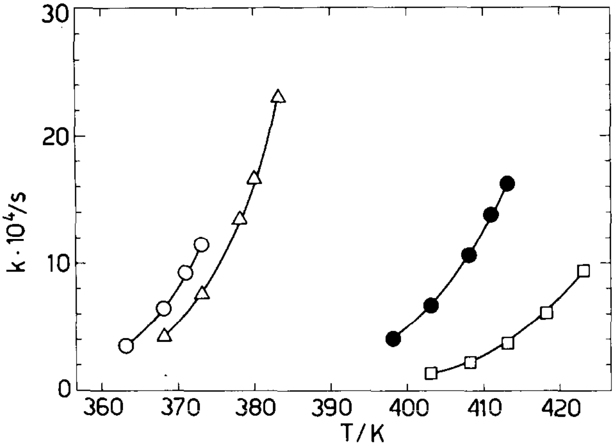


Fig. 2. Rate constant k against temperature for reaction (1). Symbols △, ○, □ and ● refer to complexes **I**, **II**, **III** and **IV**, respectively.

shown in Table 2 for the least squares fitting in the various $F(\alpha)$ vs. t plots. It may be deduced from Table 2 that the dehydration of the above mentioned complexes should follow the phase boundary reaction mechanism R_3, but almost as good are the random nucleation and subsequent growth

TABLE 3

The rate constants, k, derived from TG data at different temperatures in terms of the $R_{3.2}$ mechanism

Complex	T(K)	k ($\times 10^4$ s^{-1})	r	δ ($\times 10^2$)
I	368.15	4.21	0.99987	0.04
	373.15	7.62	0.99973	0.10
	378.15	13.44	0.99970	0.19
	380.15	16.66	0.99980	0.19
	383.15	23.03	0.99979	0.27
II	363.15	3.49	0.99995	0.04
	368.15	6.43	0.99995	0.08
	371.15	9.19	0.99997	0.09
	373.15	11.52	0.99997	0.11
III	403.15	1.28	0.99980	0.03
	408.15	2.19	0.99989	0.04
	413.15	3.70	0.99983	0.07
	418.15	6.02	0.99983	0.12
	423.15	9.34	0.99959	0.29
IV	398.15	4.02	0.99989	0.05
	403.15	6.63	0.99976	0.13
	408.15	10.62	0.99966	0.25
	411.15	13.80	0.99983	0.23
	413.15	16.19	0.99943	0.50

TABLE 4

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

Complex	E (kJ mol^{-1})	$\ln(A/\mathrm{s}^{-1})$	r
I	132.9 ± 0.7	35.7 ± 0.2	-0.99995
II	134.8 ± 0.8	36.7 ± 0.2	-0.99993
III	141.5 ± 2.1	33.3 ± 0.6	-0.99965
IV	127.4 ± 1.9	30.7 ± 0.5	-0.99965

mechanism (an Avrami–Erofeev law of A_2) or two-dimensional diffusion reaction mechanism, D_2 [6]. However, when the testing of the decomposition mechanism was carried out at different temperatures for reaction (1), it was deduced that the phase boundary reaction mechanism $R_{3.2}$ was clearly the best one.

Table 3 lists the rate constants, k, at various temperatures determined from TG data by means of an $R_{3.2}$ mechanism together with the values of δ and r. Figure 2 shows the temperature dependence of k for reaction (1). Kishore and Nagarajan [7] stated that in the case of the cobalt–salicylato complex the water molecules are crystalline. According to Melnik et al. [8] complex **II** contains two types of water molecules namely lattice-held and bonded. On the basis of relatively high temperatures for the loss of H_2O molecules in the DTG curves (Fig. 1), our results confirm the interpretation that water is at least partly coordinated to the metal.

Table 4 shows the activation energy, E, and logarithm of the frequency factor, A, derived from the Arrhenius plot together with the values of standard errors and correlation coefficient for the least squares fitting. The values of ΔH determined by DSC for the dehydration of complexes **I–III**, according to eqn. (1), are given in Table 5. By comparing the values of E with the corresponding enthalpy changes it can be observed that the ΔH values are nearly equal to the activation energies for complexes **I–III**. This kind of behaviour agrees with the expected pattern for endothermic solid decomposition [9]. The values of E increase as the size of the halogen atom

TABLE 5

Enthalpy changes, ΔH, for the thermal dehydration according to eqn. (1) for $\mathrm{Cu(5\text{-}XHL)_2 \cdot 3\,H_2O}$ complexes

Complex	T_{range} (K)	$T_{\mathrm{p}}^{\mathrm{a}}$ (K)	ΔH (kJ mol^{-1})
I	338–418	383.85	162.4
II	348–418	387.85	147.5
III	383–438	415.45	120.6

[a] In the DSC curve T_{p} refers to the sample temperature at the peak maximum.

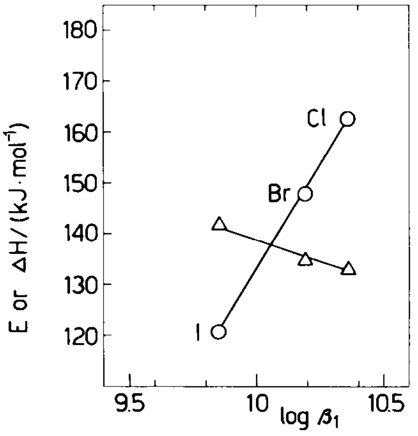


Fig. 3. Correlation between E or ΔH and log β_1 values for the complexes **I–III**. Symbols △ and ○ refer to E and ΔH values, respectively.

increases in the case of complexes **I–III**. The values of $\Delta H - E$ for complexes **I**, **II** and **III** are 29.5, 12.7 and -20.9 kJ mol^{-1}, respectively.

Figure 3 shows the correlation between the values of E or ΔH and the values of the logarithm of stability constant β_1 for complexes **I–III**. Stability constants for these complexes have been reported elsewhere [1].

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