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KINETICS OF THERMAL DEHYDRATION OF SOME BIS-(4-AMINOSALICYLATO)-DIAQUO COMPLEXES OF TRANSITION METAL IONS

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ABSTRACT

The kinetics of thermal dehydration of bis-(4-aminosalicylato)-diaquo complexes of VO(II), Cu(II), Ni(II), Co(II), Fe(II) and Mn(II), were studied. The activation energies and other kinetic parameters have been evaluated. The observed kinetic parameters indicate a first-order reaction. The activation energy of the thermal dehydration decreases in the order: VO(II) > Cu(II) > Co(II) > Ni(II) > Fe(II) > Mn(II), which is also the order for the covalency in the M–O bonds.

INTRODUCTION

We have been interested in salicylate complexes of transition metals because we view these as antimicrobial agents. In particular, a variety of bis-salicylato-diaquo metal complexes with transition metals have been prepared which were screened for antifungal and antibactorial activities [1–5]. In order to gain information on antimicrobial and structural activity relationships, it was thought worthy to undertake thermogravimetric studies of metal chelates of salicylic acids. As an extension of previous efforts [6–10], the present report deals with the kinetics of the thermal decomposition of VO(II), Cu(II), Ni(II), Co(II), Fe(II) and Mn(II) complexes of 4-aminosalicylic acid (4ASA).

EXPERIMENTAL

The complexes were prepared following a method described elsewhere [11]. Equimolar solutions of metal salts and 4ASA were prepared and mixed in the stoichiometric ratio $M/L = 1:2$. The solid complexes obtained were washed thoroughly with ethanol, dried, and recrystallized from dimethyl formamide.

All the reagents used were of BDH AnalaR grade.

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Elemental analyses

The metal content was estimated by conventional methods [12]. Carbon, hydrogen and nitrogen analyses were carried out on a Colemann CHN analyser 29. The results of elemental analyses are reported in Table 1.

TABLE 1

Analytical data for bis-(4-aminosalicylato)-diaquo complexes

Complex	Colour	M%		C%		H%		N%	
		Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
$Cu(4ASA)_2 \cdot 2H_2O$	Dark green	15.74	15.88	41.63	42.10	3.96	4.10	6.94	7.16
$Ni(4ASA)_2 \cdot 2H_2O$	Dark green	14.72	15.29	42.14	41.97	4.01	3.92	7.02	7.20
$Co(4ASA)_2 \cdot 2H_2O$	Mauve	14.77	15.26	42.11	42.88	4.01	4.14	7.01	7.30
$Mn(4ASA)_2 \cdot 2H_2O$	Brown	13.91	13.58	42.54	42.48	4.05	4.09	7.09	7.18
$Fe(4ASA)_2 \cdot 2H_2O$	Dark brown	14.10	14.38	42.44	41.98	4.04	4.28	7.07	7.28
$VO(4ASA)_2 \cdot 2H_2O$	Dark brown	16.44	15.99	41.28	41.79	3.93	4.08	6.88	7.04

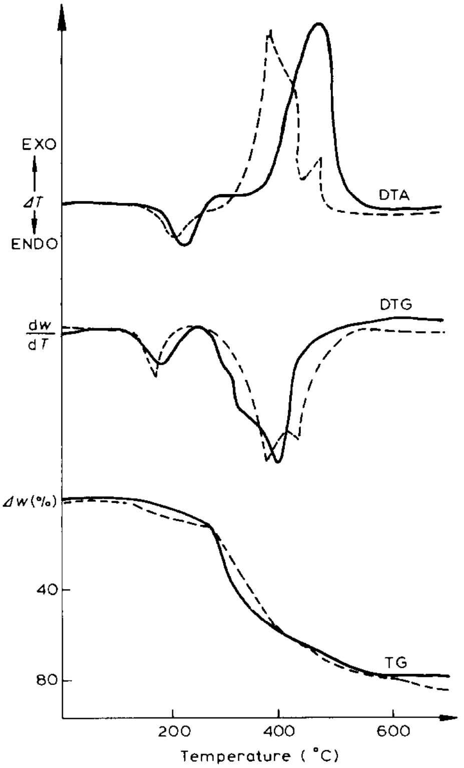

Fig. 1. TG, DTG and DTA curves for bis-(4-aminosalicylato)-diaquo complexes: (———) Cu(II); (------) Ni(II).

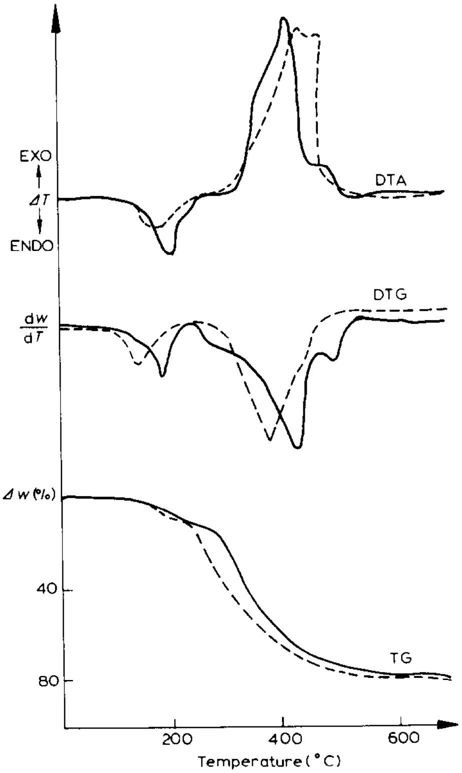

Fig. 2. TG, DTG and DTA curves for bis-(4-aminosalicylato)-diaquo complexes: (———) Co(II); (------) Mn(II).

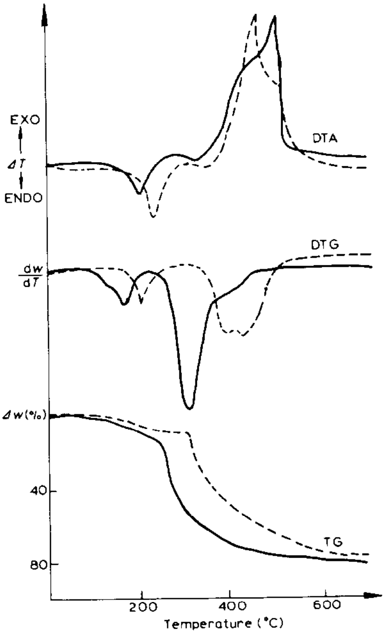

Fig. 3. TG, DTG and DTA curves for bis-(4-aminosalicylato)-diaquo complexes: (———) Fe(II); (------) VO(II).

TABLE 2

Characteristic IR frequencies for bis-(4-aminosalicylato)-diaquo complexes

Assignment	4ASA	Bis-(4-aminosalicylato)-diaquo complexes of [a]					
		Cu(II)	Ni(II)	Co(II)	Mn(II)	Fe(II)	VO(II)
νCOO^- asym.	1660 S	1620 S	1610 S	1622 S	1625 S	1625 S	1635 S
νCOO^- sym.	1470 S	1442 S	1438 S	1450 S	1455 S	1465 S	1455 S
νO-H Str. [b]	2400-3700 (3300 Sb)	2800-3650 (3290 Sb)	2700-3660 (3200 Sb)	2700-3690 (3280 Sb)	2680-3675 (3310 Sb)	2790-3650 (3215 Sb)	2750-3700 (3320 Sb)
δOH	1282 S	1282 S	1270 S	1306 S	1306 S	1287 S	1294 S
$\delta^+ H_2O$ rocking	–	880 S	850 S	850 S	835 S	828 S	885 S
ν(M-O)+(C-C)	–	505 Wb	515 m	509 Sh	510 mb	516 W	520 Sh
ν(M-O)+ring def.	–	440 Sh	460 W	425 m	420 Wb	430 m	440 m

[a] S = Strong, b = broad, W = weak, m = medium, Sh = shoulder.

[b] In some cases broad bands of the O-H stretching frequency (2400-3700 cm^{-1}) overlapped the sharp bands of N-H (3400-3500 cm^{-1}).

Thermal analyses

Thermogravimetry (TG) was carried out on a Stanton-Redcroft recording thermobalance (HT-model) of 1 mg sensitivity in static air with a heating rate of 4°C min^{-1}. The chart speed was maintained at 3 in. h^{-1}. All the samples were of the same particle size and were packed as uniformly as possible in a platinum crucible of appropriate size. The same platinum crucible was used throughout all the experiments.

A differential thermal analysis (DTA) assembly with an F and M Scientific 240 Hewlett-Packard temperature programmer, and a Platinet-II thermocouple (Engelhard, U.S.A.) were used. DTA curves were recorded by a Rikadenki Kogyo recorder in static air at a heating rate of 4°C min^{-1}. Alumina was used as a standard reference material.

The TG, DTG and DTA results are shown in Figs. 1–3.

IR spectra

The presence of the ligand and water molecules in the complexes was identified by IR spectroscopy, using a Perkin-Elmer Model 377 spectrophotometer in KBr matrix.

The characteristic band positions are given in Table 2.

RESULTS AND DISCUSSION

Stoichiometry and structure

The results of the elemental analyses (Table 1) indicate that the complexes formed had the composition $ML_2 \cdot 2H_2O$ where M represents VO(II), Cu(II), Ni(II), Co(II), Fe(II) or Mn(II), and L represents the anion of 4ASA.

The IR spectrum of the solid 4ASA is almost identical to that of its complexes in the region 2000–625 cm^{-1}. The frequencies of most interest with regard to structure are the C–O and O–H vibrations. The ν(C=O) band at 1660 cm^{-1} is shifted to a lower frequency (~ 1610 cm^{-1}) in all the complexes showing that complexation has taken place through the carboxyl group [13,14]. The appearance of new bands in the neighbourhood of 800 cm^{-1} in all the complexes shows that the water molecules are coordinated to the metal ion [15–18]. The band at ~ 315 cm^{-1} confirms the presence of coordinated water [19]. This is further borne out by the thermal decomposition data (Figs. 1–3). It may also be noted that the O–H (phenolic) bending peak at 1300 cm^{-1} remained almost at the same position for both 4ASA and its complexes. This shows that there is no loss of proton by the phenolic OH group upon coordination.

All the complexes are insoluble in water and common organic solvents, suggesting a polymeric structure for each of them. Because of their insolubility in common organic solvents, the extent of polymerization could not be determined. Earlier reported data on magnetic susceptibility and electronic spectra indicated octahedral stereochemistry for all the complexes [20]. The thermal decomposition would appear to be consistent with this type of structure and would suggest that the water molecules are directly bonded to the metal ion along with two 4ASA molecules to give a coordination number of six for each of the metal(II) ions.

A perusal of Table 2 shows that the difference in carboxylic group frequency follows the order: VO(II) > Cu(II) > Co(II) > Ni(II) > Fe(II) > Mn(II), which may be treated as the order of covalency in the M–O bonds.

Kinetic parameters

Taking into account the complexity of the thermal decomposition of the metal complexes, an attempt was made to select an appropriate method for determining various kinetic parameters of the thermal decomposition of the complexes. The methods of Horowitz and Metzger [21] and Fuoss et al. [22] were found to be suitable for this purpose.

Various kinetic parameters for the thermal dehydration reactions (the rate-determining step) have been evaluated. However, the kinetic parameters of pyrolysis of the dehydrated complexes could not be completed due to the absence of an exact inflection point, as the steps of pyrolysis were overlapped due to rapid thermal decomposition.

Determination of order of reaction

The order of reaction, n, was determined by applying the Horowitz and Metzger [21] equation, $CS = (n)^{1/(1-n)}$, where CS is the weight fraction of the substance present at the peak temperature T_s (the DTG peak temperature).

The results presented in Table 3 indicate that in all cases the order of the

TABLE 3

Kinetic data for the thermal dehydration of bis-(4-aminosalicylato)-diaquo complexes

Complex	Dehydration temp. range (°C)	T_i (K)	W^a	W_i	F(m)	(dw/dt) (mg °C^{-1})
(I) $Cu(4ASA)_2 \cdot 2H_2O$	100–250 ± 2	473	8.75	2.75	0.314	0.125
(II) $Ni(4ASA)_2 \cdot 2H_2O$	90–220 ± 4	453	9.00	3.00	0.333	0.125
(III) $Co(4ASA)_2 \cdot 2H_2O$	100–240 ± 2	453	9.00	3.50	0.388	0.150
(IV) $Mn(4ASA)_2 \cdot 2H_2O$	80–210 ± 3	413	9.25	3.50	0.378	0.150
(V) $Fe(4ASA)_2 \cdot 2H_2O$	80–220 ± 2	433	9.00	3.25	0.361	0.125
(VI) $VO(4ASA)_2 \cdot 2H_2O$	120–270 ± 3	473	8.75	2.75	0.134	0.150

[a] W is a total weight loss in the dehydration step.

dehydration reaction corresponding to the escape of water molecules is unity, showing that the dehydration follows first-order kinetics.

Evaluation of other kinetic parameters

For first-order kinetics the Fuoss et al. [22] method is employed to evaluate the activation energy, E^*, and frequency factor, Z, using expressions (a) and (b)

$$E^* = \frac{R/T_i^2}{W_i}\left(\frac{\mathrm{d}w}{\mathrm{d}T}\right)_i \tag{a}$$

$$Z = \frac{a}{W_i}\left(\frac{\mathrm{d}w}{\mathrm{d}T}\right)\exp\left(E^*/RT_i\right) \tag{b}$$

where the terms have their usual meanings [22].

Activation entropy, S^*, free energy of activation, G^*, and the specific reaction rate constant, K_r, have been calculated using their interrelationships [23] given in eqns. (c), (d) and (e), respectively

$$S^* = (\log Zh/kT)R \tag{c}$$

$$G^* = E^* - T_i S^* \tag{d}$$

$$K_r = z\exp\left(-E^*/RT_i\right) \tag{e}$$

In eqn. (c), k and h are the Boltzmann and Planck constants, respectively. The kinetic parameters thus obtained are presented in Table 4.

A perusal of Table 4 shows that the activation energies for the splitting of H_2O–M bonds lie around 14.24 kcal mol^{-1}, with an estimated uncertainty of ± 0.5 kcal mol^{-1}. These values are comparable to the generally accepted values of the activation energy of the dehydration reaction [24].

The activation energy of the thermal dehydration reaction of the complexes has been found to decrease roughly in the order: Mn(II) < Fe(II) <

TABLE 4

Kinetic parameters for the thermal dehydration of bis-(4-aminosalicylato)-diaquo complexes [a]

Complex	E^*	H^*	S^*	G^*	K_r
(I) $Cu(4ASA)_2 \cdot 2H_2O$	20.206	19.292	−12.27	26.00	3.03×10^{-3}
(II) $Ni(4ASA)_2 \cdot 2H_2O$	16.989	16.114	−14.57	23.59	2.77×10^{-3}
(III) $Co(4ASA)_2 \cdot 2H_2O$	17.475	16.600	−14.08	23.85	2.85×10^{-3}
(IV) $Mn(4ASA)_2 \cdot 2H_2O$	14.525	13.727	−15.48	20.91	2.85×10^{-3}
(V) $Fe(4ASA)_2 \cdot 2H_2O$	14.328	13.492	−16.51	21.48	2.56×10^{-3}
(VI) $VO(4ASA)_2 \cdot 2H_2O$	24.248	23.334	−08.40	28.22	3.63×10^{-3}

[a] E^* = Activation energy (kcal mol^{-1}), H^* = activation enthalpy (kcal mol^{-1}), S^* = activation entropy (e.u.), G^* = free energy of activation (kcal mol^{-1}), K_r = specific reaction rate (su^{-1}).

Ni(II) < Co(II) < Cu(II) < VO(II). This follows the same order as the binding strength of the water molecules to the metal ion. These effects suggest that the coordinated water molecules tend to be liberated in the aforementioned sequence.

The enthalpy of activation, H^*, has been evaluated from the relationship

$$H^* = E^* - KT_i \qquad \text{(f)}$$

The values of E^* and H^* differ by an average of 1.00 kcal mol^{-1}. This small difference could not be differentiated experimentally and we can safely say that E^* and H^* are equivalent. The error limit in the values of H^* is ± 0.5 kcal mol^{-1}.

It may be useful to compare the thermodynamic functions for the thermal dehydration of 4ASA complexes, which fulfil a mutual linear relation. This can be expressed for our purposes as

$$S^* = \alpha + \beta G^* \qquad \text{(g)}$$

The coefficients of eqn. (g) were computed by the least-squares method. The value of the correlation coefficient (0.99) indicates that the method of least squares is applicable and that the correlation of S^* and G^* is genuine (Fig. 4).

An attempt has also been made to calculate the isokinetic temperature β from the relationship

$$H^* = H_0^* + \beta S^* \qquad \text{(h)}$$

A straight-line graph obtained between H^* and S^* indicates that the correlation of H^* and S^* is genuine (Fig. 4).

The negative value of the activation entropy suggests that the thermal

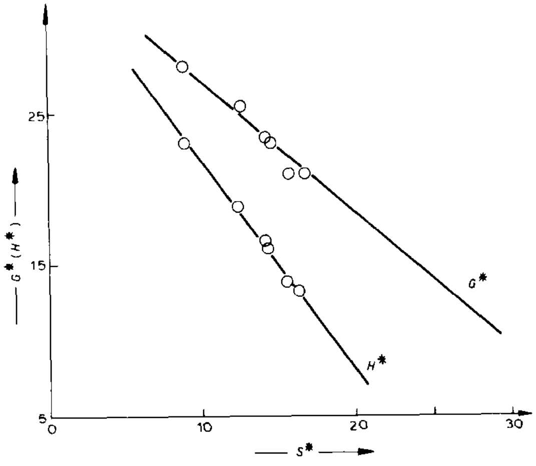

Fig. 4. Correlation of S^* with G^* (H^*).

dehydration reaction is slower. This is clearly borne out from the shape of the corresponding TG curve.

The values of all the other kinetic parameters (Table 4) obtained are within the range usually observed for a first-order reaction [10,25]. Thus, it can be concluded that the thermal dehydration of these complexes is a first-order reaction.

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