

KINETICS OF THERMAL DEHYDRATION OF SOME BIS-SALICYLATO-DIAQUO COMPLEXES OF TRANSITION METAL IONS

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The kinetics of thermal dehydration of bis-salicylato-diaquo complexes of VO(II), Cu(II), Ni(II), Co(II), Fe(II), Mn(II) and Zn(II) were studied. The activation energies and other kinetic parameters were evaluated. The observed kinetic parameters indicate first-order reactions. The activation energy of the thermal dehydration decreases in the sequence VO(II) > Cu(II) > Zn(II) > Co(II) > Ni(II) > Fe(II) > Mn(II), which is also the sequence for the difference in carboxyl group IR frequency.

Much effort has been devoted to the preparation and study of metal complexes of salicylic and nuclear-substituted salicylic acids, partly because of the importance of this class of compounds as analytical agents and partly because of their antimicrobial activity. In contrast, only a little is known concerning their thermal behaviour. In view of the importance of the antimicrobial and structure-activity relationships, it was thought worthwhile to undertake thermogravimetric studies of metal chelates of salicylic acids.

In previous paper [1–4] we have reported the preparation and a brief description of the thermogravimetric behaviour of the salicylic acid chelates of VO(II), Cu(II), Ni(II), Co(II), Fe(II), Mn(II) and Zn(II). Since most of these chelates are thermally stable and insensitive to air, they provide an opportunity for study of the kinetics of their thermal behaviour. The detailed kinetic studies are expected to provide important information supplementing that on the thermal stabilities of metal salicylates and their decomposition pathways. Further, such a study will help in the preparation of new compounds with versatile microbial activity.

As an extension of our previous kinetic studies concerning the thermal dehydration of VO(II), Zn(II) and Fe(II) salicylates [20], we now report on the thermal dehydration of the analogous salicylic acid complexes of Cu(II), Ni(II), Co(II) and Mn(II). Results obtained in the earlier study [1] are included for comparison.

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Experimental

The complexes were prepared following the method described elsewhere [5]. Equimolar solutions of metal salts and salicylic acid 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 dimethylformamide. All reagents were of BDH AnalaR grade.

Elemental analyses

The metal content was estimated by conventional methods [6]. Carbon, hydrogen and nitrogen analyses were carried out on a Colemann 29 CHN analyser. The results of elemental analyses are recorded in Table 1.

Table 1 Analytical data on bis-salicylato-diaquo complexes

Complex	Colour	% Yield	M %		C %		H %	
			Calc.	Found	Calc.	Found	Calc.	Found
(I) $\text{Cu}(\text{SA})_2 \cdot 2 \text{H}_2\text{O}$	green	70	17.01	16.90	44.97	45.10	3.74	3.59
(II) $\text{Ni}(\text{SA})_2 \cdot 2 \text{H}_2\text{O}$	light green	75	15.91	16.00	45.56	45.16	3.79	3.92
(III) $\text{Co}(\text{SA})_2 \cdot 2 \text{H}_2\text{O}$	pink	80	15.97	15.90	45.53	46.04	3.79	3.84
(IV) $\text{Mn}(\text{SA})_2 \cdot 2 \text{H}_2\text{O}$	light brown	65	15.05	15.60	46.03	45.84	3.83	4.08
(V) $\text{Fe}(\text{SA})_2 \cdot 2 \text{H}_2\text{O}$	dark green	60	15.26	15.10	45.92	45.80	3.82	3.91
(VI) $\text{VO}(\text{SA})_2 \cdot 2 \text{H}_2\text{O}$	dark green	60	17.75	17.60	44.57	44.38	3.71	3.81
(VII) $\text{Zn}(\text{SA})_2 \cdot 2 \text{H}_2\text{O}$	dirty white	85	17.41	17.08	44.75	45.02	3.73	3.70

Thermal analysis

Thermogravimetry (TG) was carried out on a Stanton HT recording thermobalance of 1 mg sensitivity, in static air, at a heating rate of 4 deg/min. The chart speed was maintained at 3 inches/hr. All 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 the experiments.

The differential thermal analysis (DTA) assembly with the temperature programmer of F and M Scientific 240 Hewlett-Packard and the Platinet-II thermocouple of Engelhard U. S. A. were used. DTA curves were recorded with a Rikadenki Kogyo recorder in static air at a heating rate of 4 deg/min. Alumina was used as reference material.

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

IR spectra

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

The characteristic band positions are given in Table 2.

Table 2 Characteristic IR group frequencies for bis-salicylato-diaquo complexes

Assignment	SA	Cu(II)	Ni(II)	Co(II)	Mn(II)	Fe(II)	VO(II)	Zn(II)
ν COO asym.	1660 (S)	1620 (S)	1630 (S)	1620 (S)	1605 (S)	1630 (S)	1630 (S)	1630 (S)
ν COO sym.	1450 (S)	1400 (S)	1420 (S)	1410 (S)	1400 (S)	1435 (S)	1405 (S)	1410 (S)
ν O-H stretch	2600-3600 (3300) (Sb)	2700-3660 (3380) (Sb)	3000-3670 (3390) (Sb)	3000-3650 (3500) (Sb)	2800-3655 (3400) (Sb)	2900-3640 (3410) (Sb)	2700-3665 (3340) (Sb)	3650-2800 (3400) (Sb)
δ H ₂ O rocking	-	870 (S)	860 (S)	860 (S)	850 (S)	855 (S)	898 (S)	855 (S)
ν (M-O) + (C-C)	-	596 (Sh)	585 (Sh)	540 (mb)	580 (w)	565 (Sh)	570 (m)	575 (m)
ν (M-O) + ring deform.	-	455 (m)	470 (wb)	425 (m)	475 (mb)	450 (w)	430 (S)	435 (w)
Δ C=O	-	220	210	210	205	195	225	220

Δ C=O = ν COO asym - ν COO sym; S = sharp, Sb = sharp and broad, Sh = shoulder, m = medium, mb = medium and broad, w = weak, wb = weak and broad.

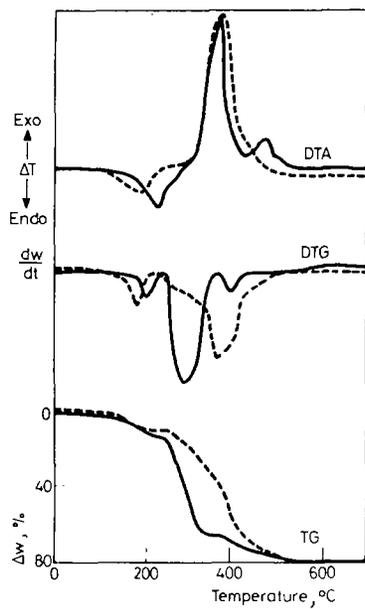


Fig. 1

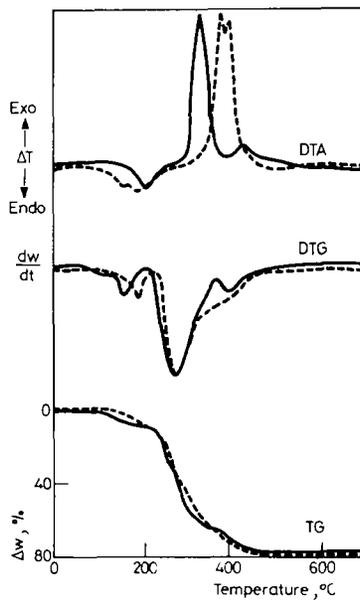


Fig. 2

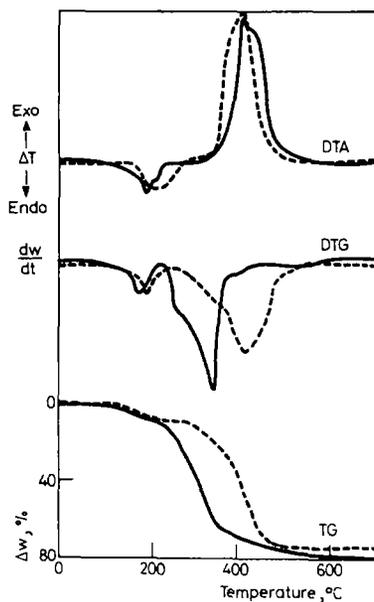


Fig. 3

Results and discussion

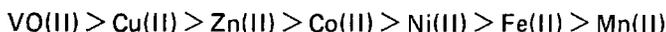
Stoichiometry and structure

The results of elemental analyses (Table 1) indicate that the complexes formed have the composition $ML_2 \cdot 2 H_2O$, where M stands for VO(II), Cu(II), Ni(II), Co(II), Fe(II), Mn(II) and Zn(II), and L for the salicylate anion.

The infrared spectrum of solid salicylic acid is almost identical to those of its complexes in the region $2000-625 \text{ cm}^{-1}$. The frequencies of most interest with regard to structure are those of the C—O and O—H vibrations. The $\nu(\text{C}=\text{O})$ band at 1650 cm^{-1} is shifted to lower frequency ($\approx 1570 \text{ cm}^{-1}$) in all the complexes, showing that complexation takes place through the carboxyl group [7, 8]. The infrared spectra also show that the $\nu(\text{OH})$ band shifts from 3240 cm^{-1} for salicylic acid to $\approx 3500 \text{ cm}^{-1}$ for the complexes, indicating the absence of hydrogen-bonding [9]. The appearance of new bands in the neighbourhood of 800 cm^{-1} for all the complexes shows that the water molecules are coordinated to the metal ion [10–12]. A band at $\approx 315 \text{ cm}^{-1}$ confirms the presence of coordinated water [13]. The presence of coordinated water is further borne out by the thermal decomposition data (Figs 1–3). It may also be noted that the OH (phenolic) bending peak at 1300 cm^{-1} is at almost the same position for salicylic acid 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 data on the magnetic susceptibility and electronic spectra, except for Zn(II), indicated octahedral stereochemistry for all the complexes [14]. 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 salicylate molecules, to give a coordination number of six for each of the metal(II) ions.

Table 2 shows that the difference in carboxyl group frequency, $\Delta_{C=O}$, follows the sequence



which may be treated as the order of covalency of the M-L bond.

Kinetic parameters

Taking into account the complexity of the thermal decompositions of the metal complexes, an attempt was made to select an appropriate method for determining the various kinetic parameters of thermal decomposition. The methods of Horowitz and Metzger [15] and Fuoss et al. [16] were found to be suitable for this purpose.

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

Determination of order of reaction

The order of reaction n was determined by applying the Horowitz and Metzger [15] equation $C_s = (n)^{1/(1-n)}$, where C_s is the weight fraction of substance present at the peak temperature T_s (the DTG peak temperature). C_s is given by

$$-C_s = \frac{W - W_t^f}{W_0 - W_t^f}$$

where W = weight at temperature T_s , W_0 = initial weight of the substance and W_t^f = final weight of the substance.

The order of thermal dehydration in each is obtained by comparing the C_s value yielded by the above method with the values given in the Horowitz and Metzger [15] table. The order is calculated to be unity.

The results (C_s) presented in Table 3 column 6 indicate that in all cases the order of the dehydration reaction corresponding to the escape of water molecules is unity, showing that the dehydration follows first-order kinetics.

Table 3 Kinetic data on thermal dehydrations of bis-salicylato-diaquo complexes

Complex	Dehydration temperature range, °C	T_i , K	W^a	W_i	C_s	$(dw/dt)_i$, mg/°C
(1) $\text{Cu}(\text{SA})_2 \cdot 2 \text{H}_2\text{O}$	100–240±4	473	9.50	3.00	0.315	0.125
(2) $\text{Ni}(\text{SA})_2 \cdot 2 \text{H}_2\text{O}$	80–220±2	453	9.60	3.10	0.322	0.125
(3) $\text{Co}(\text{SA})_2 \cdot 2 \text{H}_2\text{O}$	100–220±4	433	9.60	3.35	0.348	0.150
(4) $\text{Mn}(\text{SA})_2 \cdot 2 \text{H}_2\text{O}$	80–210±2	453	9.50	3.50	0.368	0.125
(5) $\text{Fe}(\text{SA})_2 \cdot 2 \text{H}_2\text{O}$	80–220±2	433	9.75	3.75	0.384	0.150
(6) $\text{VO}(\text{SA})_2 \cdot 2 \text{H}_2\text{O}$	110–260±4	473	9.50	3.25	0.342	0.162
(7) $\text{Zn}(\text{SA})_2 \cdot 2 \text{H}_2\text{O}$	100–240±4	463	9.50	3.50	0.368	0.150

^a W : total weight loss in dehydration step.

Evaluation of other kinetic parameters

For first-order kinetics, the Fuoss method [16] is employed to evaluate the activation energy E^* and the frequency factor Z , using expressions (a) and (b):

$$E^* = \frac{R}{T_i^2} \left(\frac{dW}{dT} \right)_i \quad (\text{a})$$

$$Z = \frac{a}{W_i} \left(\frac{dW}{dT} \right) \exp \frac{E^*}{RT_i} \quad (\text{b})$$

where the terms have their usual meaning [16].

The activation entropy S^* , the free energy of activation G^* and the specific reaction rate constant K_r were calculated using the relationships [17] given in Eqs (c), (d) and (e):

$$S^* = \left(\log \frac{Zh}{kT} \right) R \quad (\text{c})$$

$$G^* = E^* - T_i S^* \quad (\text{d})$$

$$K_r = Z \exp - \frac{E^*}{RT_i} \quad (\text{e})$$

In Eq. (c) k and h are the Boltzmann and Planck constants, respectively.

The kinetic parameters so obtained are presented in Table 4. The activation energies for splitting of the $\text{H}_2\text{O}-\text{M}$ bonds lie in the range 60–92 kJ/mol, with an estimated uncertainty of ±2.1 J/mol. The values are comparable to the usual values for the activation energies of dehydration reactions [18].

The activation energy of thermal dehydration of the complexes was found to decrease in the sequence:



This is the sequence of binding strength of the water molecules to the metal ion, which suggests that the coordinated water molecules tend to be liberated in the above sequence.

The enthalpy of activation H^* was evaluated from the relationship:

$$H^* = E^* - RT_i \quad (f)$$

The values of E^* and H^* differ by an average of 4.2 kJ/mol. This small difference could not be differentiated experimentally and we could safely say that E^* and H^* are equivalent. The error limit in the H^* values is ± 2.1 kJ/mol.

It may be useful to compare the thermodynamic functions for the thermal dehydration of salicylic acid complexes, which fit a linear relation. This can be expressed for our purposes as:

$$S^* = \alpha + \beta G^* \quad (g)$$

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

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

$$H^* = H_0^* + \beta S^* \quad (h)$$

A straight line graph between H^* and S^* (Fig. 4) indicates that the correlation of H^* and S^* is genuine [19].

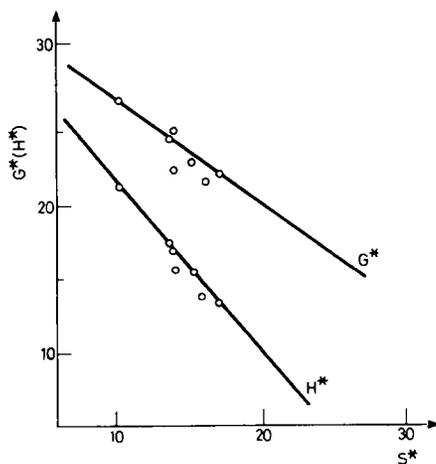


Fig. 4

Data for all other salicylic acid complexes fall on the same linear plot, indicating their similar dehydration behaviour.

The negative entropy of activation suggests that the thermal dehydration reaction is slower. This is clearly borne out by the shape of the corresponding TG curve.

Table 4 Kinetic parameters of the thermal dehydration of the complexes

Complex	E^* , kJ mol ⁻¹	H^* , kJ mol ⁻¹	S^* , J mol ⁻¹ °C ⁻¹	G^* , kJ mol ⁻¹	Kr , s ⁻¹
(1) Cu(SA) ₂ · 2 H ₂ O	77.50	73.58	377.48	104.97	2.77 × 10 ⁻³
(2) Ni(SA) ₂ · 2 H ₂ O	68.79	65.46	359.60	97.44	2.68 × 10 ⁻³
(3) Co(SA) ₂ · 2 H ₂ O	69.79	66.20	372.71	95.185	2.98 × 10 ⁻³
(4) Mn(SA) ₂ · 2 H ₂ O	60.93	57.18	331.89	93.17	2.38 × 10 ⁻³
(5) Fe(SA) ₂ · 2 H ₂ O	62.34	58.80	346.32	91.16	2.66 × 10 ⁻³
(6) VO(SA) ₂ · 2 H ₂ O	92.71	88.79	426.80	113.09	3.32 × 10 ⁻³
(7) Zn(SA) ₂ · 2 H ₂ O	76.54	72.54	379.04	102.96	2.82 × 10 ⁻³

E = energy of activation, H^* = enthalpy of activation, S^* = activation entropy, G^* = free energy of activation, Kr = specific reaction rate.

The values of all the other kinetic parameters (Table 4) are within the range usually observed for first-order reactions [20]. Thus, it can be concluded that the thermal dehydration of each of these complexes is a first-order reaction.

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Zusammenfassung – Die Kinetik der thermischen Dehydratisierung von Bis-salicylato-diaquo-Komplexen von VO(II), Cu(II), Ni(II), Co(II), Fe(II), Mn(II) und Zn(II) wurden untersucht. Aktivierungsenergien und andere kinetische Parameter wurden bestimmt. Die beobachteten kinetischen Parameter weisen auf Reaktionen erster Ordnung hin. Die Aktivierungsenergie der thermischen Dehydratisierung nimmt in der Reihenfolge VO(II) > Cu(II) > Zn(II) > Co(II) > Ni(II) > Fe(II) > Mn(II) ab. In der gleichen Reihenfolge ändert sich auch die IR-Frequenz der Carbonylgruppe.

Резюме – Изучена кинетика реакций термической дегидратации диакво-бис-салицилатных комплексов двухвалентных ванадила, меди, никеля, кобальта, железа, марганца и цинка. Оценены энергии активации и некоторые другие кинетические параметры, свидетельствующие о реакциях первого порядка. Энергия активации процесса термической дегидратации уменьшается в ряду VO(II) > Cu(II) > Zn(II) > Co(II) > Ni(II) > Fe(II) > Mn(II). Эта же последовательность коррелируется с наблюдаемым различием частот колебаний карбонильной группы в ИК спектрах.