DEHYDRATION KINETICS OF THE COPPER(II) CHELATE OF SALICYLHYDRAZIDE: A THERMOGRAVIMETRIC STUDY

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ABSTRACT

Weight loss experiments for the copper(II) chelate of salicylhydrazide (Cu(II)-SH) were followed by thermogravimetry (TG). The curves were analysed by the Horowitz–Metzger and Coats–Redfern methods. Refined values of the kinetic and thermodynamic variables were obtained by regression analysis. The kinetic variables for the thermal dehydration estimated by these methods were found to be in close agreement, which indicates that the methods are best suited for thermal dehydration studies. The results were computed using an ICIM-6000 and a program designed by the authors.

INTRODUCTION

Benzohydrazides play an extremely important role in the structure and function of a number of biologically significant molecules, by virtue of their being coordinated to metal ions. Very few metal chelates of benzohydrazides have been reported which show a linear relationship between the thermal stability of the metal benzohydrazides and the structure of the chelating benzohydrazides. In an attempt to develop such a structure–activity relationship, we have recently reported the thermal behaviour of metal chelates of 5-nitrosalicylhydrazide [1,2]. The present study investigates the thermal behaviour and estimates the kinetic and thermodynamic variables for the thermal dehydration of the Cu^{II} chelate of salicylhydrazide (SH). The Horowitz–Metzger [3] and Coats–Redfern [4] methods are used for this purpose, and precise values are then obtained by least-squares regression analysis of the data [5].

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Preparation of Cu^{II}-salicyl hydrazide (Cu(II)-SH)

The Cu^{II}-salicylhydrazide (Cu(II)-SH) was prepared by a method described elsewhere [6]. A hot aqueous solution of Cu^{II}-perchlorate was mixed with ethanolic solution of the ligand in a 1 : 2 (M : L) ratio, with the ligand in slight excess. The mixture was refluxed for 4–5 h and the volume of the solution was reduced by one-half. The product, which separated either immediately or when the reaction mixture was set aside for some hours, was washed with hot water, then ethanol, and dried in vacuum over silica gel (yield ca. 75–80%).

Analytical procedures

Microanalysis for carbon, hydrogen and nitrogen was performed on a Collmann CHN analyser-29. Copper was estimated by the standard iodometric procedure [7]. Analytical data are given in Table 1.

Thermal measurements

Thermogravimetry (TG) was carried out on a Stanton Redcroft recording thermobalance (HT-model) having a sensitivity of 1 mg in static air with a heating rate of $4°C min^{-1}$. The chart speed was maintained at 3 in h^{-1}. The sample (100 mg) was homogenized by sieving below 100 mesh and was packed as uniformly as possible in a platinum crucible of appropriate size. The same platinum crucible was used for all the experiments.

Presentation of the data

Various observations made in this investigation are presented in Figs. 1–3 and summarized in Tables 1–7. In Tables 1 and 5 the range of the thermal

TABLE 1

Thermoanalytical data for the decomposition of $CuSH_2 \cdot 2H_2O$ [a]

Decomposition period (steps)	Temp. range ($°C$)	Colour [b]	Composition [c] of residue	Weight loss (%) [c]	
				Calc.	Obs.
I	180–320	OG	$Cu(SH)_2$	8.97	10.08
II	330–520	DG	CuSH	46.58	50.00
III	525–800	BB	CuO	84.18	84.25

[a] All experiments were carried out in air at a heating rate of $4°C$.
[b] OG, Olive green; DG, dark green; BB, brownish black.
[c] The observed per cent weight losses in steps I and II are more than the calculated losses, which may be attributed to the simultaneous loss of water molecules and the loss of the salicylhydrazide moieties.
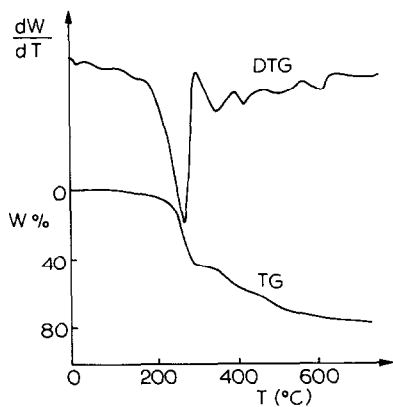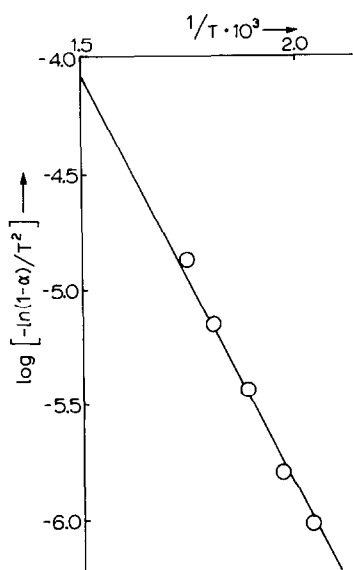
Fig. 1. TG and DTG curves for $CuSH_2 \cdot 2H_2O$.

Fig. 2. Coats–Redfern treatment for $CuSH_2 \cdot 2H_2O$.
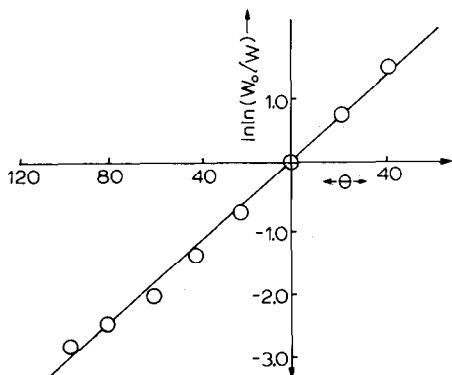

Fig. 3. Horowitz–Metzger treatment for $CuSH_2 \cdot 2H_2O$.

TABLE 2

TG horizontal, maxima and range of DTG peaks of $CuSH_2 \cdot 2H_2O$ complex [a]

Decomposition stage (step)	Horizontal TG range ($^\circ$C)	Maximum of DTG curve ($^\circ$C)	Range of DTG effect ($^\circ$C)	Remarks
I	180–320	275	260–325	Loss of two water molecules
II	330–520	380, 460	325–425; 425–460	Loss of one SH and its simultaneous decomposition
III	525–800	610	595–630	Loss of two SH moieties and their subsequent decomposition

[a] All experiments were carried out in air at a heating rate of 4°C min^{-1}.

TABLE 3

Coats–Redfern treatment for the dehydration of $Cu(SH)_2 \cdot 2H_2O$

Stage no.	Temp. (K)	$1/T \times 10^3$	W/WT	$\log_{10}\{[-\ln(1-\alpha)]/T^2\}$
1	453	2.20750	0.08235	−6.37798
2	473	2.11416	0.11764	−6.25224
3	493	2.02839	0.21176	−6.00919
4	513	1.94931	0.35294	−5.78142
5	533	1.87617	0.64705	−5.43581
6	553	1.80831	0.88235	−5.15502
7	574	1.74520	0.98823	−4.86866

TABLE 4

Horowitz–Metzger treatment for the dehydration of $Cu(SH)_2 \cdot 2H_2O$

Stage no.	Temp. (K)	θ	W	W_0/W	$\ln\ln(W_0/W)$
1	373	−160	113.4	1.01190	−4.43673
2	393	−140	112.05	1.02409	−3.73762
3	413	−120	110.7	1.03658	−3.32612
4	433	−100	108.0	1.0625	−2.80305
5	453	−80	105.3	1.08974	−2.45407
6	473	−60	101.25	1.13333	−2.07813
7	493	−40	90.45	1.26865	−1.43565
8	513	−20	74.25	1.54545	−0.83167
9	533	0	40.5	2.83333	+0.04061
10	553	+20	13.5	8.5	+0.76083
11	573	+40	1.33	8.5	+1.4912513

TABLE 5

Regression analysis: least-squares command for the data obtained for thermal dehydration of $Cu(SH)_2 \cdot 2H_2O$ from the Horowitz–Metzger and Coats–Redfern methods

Stage no.	Variable	Computational method	
		Horowitz–Metzger	Coats–Redfern
1	n	11	7
2	ΣX	−660.00	13.73
3	ΣY	−18.81	−39.88
4	ΣXY	2382.52	−78.77
5	ΣX^2	83600.00	27.09
6	ΣY^2	68.47	229.13
7	$(\Sigma X)^2$	43600.00	188.49
8	$(\Sigma Y)^2$	353.83	1590.44
9	R	0.992	0.995

TABLE 6

Kinetic and thermodynamic variables for the thermal dehydration of $CuSH_2 \cdot 2H_2O$ [a]

Method	$E^\star$ (kJ mol^{-1})	$G^\star$ (kJ mol^{-1})	$H^\star$ (kJ mol^{-1})	$S^\star$ (J mol^{-1}K^{-1})	log A (s^{-1})	log K_γ (s^{-1})
Horowitz–Metzger	68.52	99.58	64.42	59.86	5.85	5.83
RA	(67.31)	(97.95)	(63.17)	(58.52)	(6.04)	–
Coats–Redfern	64.26	97.20	63.17	61.83	5.61	5.60
RA	(62.83)	(95.15)	(60.66)	(58.39)	(5.75)	–
Mean	65.78	97.47	62.07	67.15	5.81	5.72

[a] Values in parentheses are obtained from least-squares regression analysis.
$E^\star$, Energy of activation; $G^\star$, free energy of activation; $H^\star$, enthalpy of activation; $S^\star$, entropy of activation; K_γ, specific rate constant; A, pre-exponential factor; RA, regression analysis.

TABLE 7

Comparison of kinetic variables ($E^\star$ and log A) in copper complexes of salicylhydrazide (SH), salicylic acid (SA) and salicylhydroxamic acid (SHA)

CU complexes	$E^\star$ (kJ mol^{-1})	log A (s^{-1})	Ref.
Cu SA	77.52	6.00	23, 26
Cu SH	65.72	5.61	Present study
Cu SHA	65.97	5.78	24, 25

SA, Salicylic acid moiety; SH, salicylhydrazide moiety; SHA, salicylhydroxamic acid moiety.

decomposition and the residue left during specific stages of decomposition are given. This information is derived from Fig. 1.

The results obtained using the methods of Horowitz–Metzger [3] and Coats–Redfern [4] are recorded in Figs. 2 and 3 respectively. The data

needed for this purpose are given in Tables 3 and 4 respectively. The kinetic and thermodynamic variables estimated by these methods are given in Table 6. The results of least-squares regression analysis of the data obtained by the Coats–Redfern and Horowitz–Metzger methods is given in Table 5.

The results obtained from the present system are compared with those of similar systems; the data needed for such a comparison are given in Table 7.

RESULTS

Stoichiometry of Cu^{II}-salicylhydrazide $(Cu(SH)_2 \cdot 2H_2O)$

Preparation of the title compound was carried out following the method described by Amma and Khadikar [6]. Chemical analysis of the data indicated the formation of the bis(salicylhydrazide)-diaquo-cuperato complex. The compound was characterized by spectral and magnetochemical techniques. The following structure is suggested, in accordance with Khadikar [2].
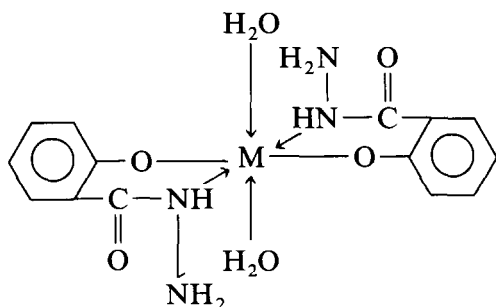
The results of thermogravimetry are consistent with this type of structure and suggest that water molecules are directly coordinated to copper together with two salicylhydrazide moieties, to give a coordination number six for the Cu^{II} ion.

Thermogravimetry of $Cu(SH)_2 \cdot 2H_2O$

The TG curve obtained for $Cu(SH)_2 \cdot 2H_2O$ is shown in Fig. 1. Direct analysis of this curve helps in estimating the weight loss associated with dehydration and decomposition. The former is estimated from weight loss up to 573 K and the latter from weight loss between 573 and 1073 K. From Fig. 1 it can be seen that the dehydration appears as a single wave whereas the decomposition appears in the form of overlapping waves.

The data in Table 1 indicate that the weight lost through the dehydration region is in accordance with the loss of two water molecules. Also, the

temperature range in which the water molecules are lost indicates that they are coordinated to the copper ion. Furthermore, the single-step dehydration indicates that both of the water molecules are equally bound to the metal ions.

Dehydration kinetics of Cu(SH)₂ · 2H₂O

The TG curve in Fig. 1 consists of two parts: the first covers the range up to 623 K and the second covers the range from 623 to 1073 K.

For analysis of the dehydration curve two methods, i.e. the Horowitz–Metzger [3] and Coats–Redfern [4] methods, were used. The data obtained in each case were analysed by least-squares regression analysis [5].

Order of thermal dehydration

The Horowitz–Metzger [3] equation $C_s = (n)^{1/1-n}$, where C_s is the weight fraction of the substance present at the DTG peak temperature (T_s) and is given by

$$C_s = W_s - W_f/W_0 - W_t \tag{1}$$

was used for estimating the order of dehydration. Here W_s stands for the weight fraction at T_s, i.e. the DTG peak temperature, and W_0 and W_f are the initial and the final weights of the substance. The order of dehydration of $CuSH_2 · 2H_2O$ is obtained by comparing the C_s value obtained by the above method with that given in the Horowitz–Metzger [3] table. The order so calculated is found to be one, which shows that the dehydration follows first-order kinetics.

Evaluation of energy of activation $(E^\star)$ and pre-exponential factor (A)

Coats–Redfern method

This method for the estimation of $E^\star$ (energy of activation) and A (the pre-exponential factor), as reviewed by Johnson and Gallagher [8], is an integral method which assumes various orders of reaction and compares the linearity in each case, to select the correct order. These orders (zero, one-half, two-thirds, and first) have been used as each of these corresponds to a simple model for solid-state decomposition. The data presented in Table 3 fit the first-order reaction well, and confirm the order obtained by the Horowitz–Metzger method. The following equation is, therefore, used to obtain the values of $E^\star$ and A for the thermal dehydration of $CuSH_2 · 2H_2O$

$$\log_{10}\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \log_{10}\left[\frac{ZR}{\beta E^\star}\left(1 - \frac{2RT}{E^\star}\right)\right] - \frac{E^\star}{2.3RT} \tag{2}$$

where β the is heating rate and α the fraction decomposed at a particular order of reaction.

By plotting the left-hand side of eqn. (2) versus $1/T$ (Fig. 2), the slope equals $-E/2.3R$. In testing the present $CuSH_2 \cdot 2H_2O$ dehydration data, the equations expressing the order 01, half and two-thirds were also plotted. However, the first-order equation was found to fit better. The evaluated $E^\star$ and A are shown in Table 6.

Horowitz–Metzger method

The Horowitz–Metzger method [3] is the most commonly used method for the estimation of $E^\star$ and A. Data needed for such estimation are given in Table 4. The expressions used for the estimation of $E^\star$ and A are as follows

$$\ln \ln(W_0/W) = (E^\star/R)T_s^2 \tag{3}$$

$$\ln(W/W_0) = (A/q) - (RT_s^2/E^\star) \exp(-E^\star/RT) \tag{4}$$

where W_0 is the initial weight; W is the weight remaining at a given temperature; T_s is the reference temperature at which dw/dt is maximum and $\theta = T - T_s$. A plot of $\ln \ln(W_0/W)$ against θ gives a straight line (Fig. 3). $E^\star$ and A are then obtained from the slope and intercept of the plot respectively and are given in Table 6.

Evaluation of thermodynamic variables

The thermodynamic variables, namely activation entropy $S^\star$, free energy of activation $G^\star$, enthalpy of activation, $H^\star$, and specific rate constant K_r, which are needed to explain the mechanism of thermal dehydration, have been calculated using their interrelationships [22], given as follows:

$$S^\star = (\log Ah/KT) \tag{5}$$

$$G^\star = E^\star - T_s S^\star \tag{6}$$

$$H^\star = E^\star - RT_s \tag{7}$$

$$K_r^\star = Z \exp(-E^\star/RT_s) \tag{8}$$

In eqn. (5), K and h are the Boltzmann constant and Planck's constant respectively.

The thermodynamic parameters thus obtained are presented in Table 6.

Regression analysis of the data obtained by the Coats–Redfern and Horowitz–Metzger methods

To obtain precise values of the kinetic and thermodynamic variables, the data obtained by the Coats–Redfern and Horowitz–Metzger methods are subjected to least-squares regression analysis. The least-squares commands for these methods are presented in Table 5, from which it can be seen that

high values of the correlation coefficient R for both the Coats–Redfern (0.995) and Horowitz–Metzger (0.992) methods show a very good linearity. The values of various kinetic and thermodynamic variables obtained from the regression analysis in each case agree well with those obtained directly from the slope of the straight-line plot. The uncertainty for $E^\star$ and $H^\star$ is ± 0.02 and ± 4.18 kJ, respectively.

DISCUSSION

The single-step thermal dehydration (Fig. 1) indicates that during thermal dehydration of $CuSH_2 \cdot 2H_2O$ two water molecules are lost simultaneously. This further suggests that the water molecules are equally bonded to the central Cu^{II} ions.

From Table 6 it can be seen that the $E^\star$ values for the dehydration of $CuSH_2 \cdot 2H_2O$ lie around 66.98 kJ mol^{-1}, with an estimated uncertainly of ± 2.1 kJ mol^{-1}. These values are the generally accepted values of activation energy of dehydration reactions [9,10].

It is interesting to note that the activation energies estimated by the Coats–Redfern and Horowitz–Metzger methods are similar. However, close examination of Table 6 indicates that the value obtained by the latter method is somewhat higher than that obtained by the former method. This is in accordance with the authors' earlier findings [11–15] as well those of other investigators [16–18].
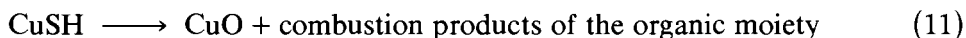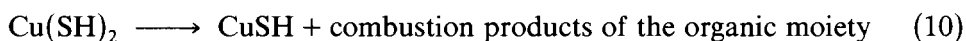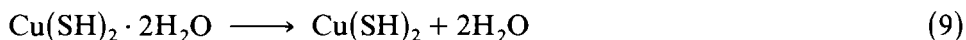
It should also be noted that the rates of thermal dehydration and decomposition cannot be solely determined by $E^\star$, as A can vary over a considerable range. It is the free energy of activation, $G^\star$, which determines the rate of reaction [19]. The higher the $G^\star$ value, the slower is the reaction rate at a given temperature. If the entropy of activation $S^\star$ is negative, the activated complex is less probable and the rate is slower [20]. Thus a large negative value for entropy of activation and a high free energy of activation denote a slow reaction. The magnitude of the negative $S^\star$ value in the present case suggests appreciable thermal dehydration of $CuSH_2 \cdot 2H_2O$, and is consistent with the shape of the TG curve.

The enthalpy of activation $H^\star$ has been evaluated using eqn. (7). The values of $E^\star$ and $H^\star$ differ by an average of 4.18 kJ mol^{-1}. This small difference could not be distinguished experimentally and we could safely say that $E^\star$ and $H^\star$ are equivalent. The error limit in the value of $H^\star$ is ± 2.1 kJ mol^{-1}.

Finally, the kinetic and thermodynamic variables given in Table 6 are found to lie within the range observed for a first-order thermal dehydration [21]. Thus it can be concluded that the thermal dehydration of $CuSH_2 \cdot 2H_2O$ follows first-order kinetics.

Mechanism of thermal dehydration and decomposition

Based on the above discussion, the general features of the thermal dehydration and decomposition can be represented by

$$Cu(SH)_2 \cdot 2H_2O \longrightarrow Cu(SH)_2 + 2H_2O \tag{9}$$

$$Cu(SH)_2 \longrightarrow CuSH + \text{combustion products of the organic moiety} \tag{10}$$

$$CuSH \longrightarrow CuO + \text{combustion products of the organic moiety} \tag{11}$$

Close examination of Fig. 1 indicates that reactions (10) and (11) are simultaneous.

Comparison with similar compounds

It is interesting to compare the results obtained for $CuSH_2 \cdot 2H_2O$ with those obtained by the authors [15] for similar organic moieties, i.e. salicylic acid (SA) and salicylhydraxamic acid (SHA); the relevant data are given in Table 7.

It is noteworthy that the $S^\star$ value for the thermal dehydration of Cu^{II}-SH is the same as that reported earlier [6,15] for Cu^{II} chelates of salicylhydroxamic acid (Cu(II)-SHA) [6,15], which indicates a mutual secondary steric influence of the side-chain (CO–NH–NH$_2$) in the vicinity of phenolic groups on dehydration. Generally, the $S^\star$ values for the dehydration of salicylhydrazide and salicylhydroxamic acid are much higher than that for salicylic acid.

CONCLUSIONS

The main conclusions are as follows:

(1) The decomposition of $CuSH_2 \cdot 2H_2O$ is a multistep process which involves dehydration followed by degradation.

(2) The identical entropy of activation for copper(II)-salicylhydrazide and copper(II)-salicylhydroxamate indicates a secondary steric effect of the side-chain: –CO–NH–NH$_2$ in metal-salicylhydrazide and –CO–NHOH in metal-salicylhydroxamates.

(3) The values of kinetic and thermodynamic variables obtained by the Coats–Redfern and Horowitz–Metzger methods are virtually identical.

REFERENCES

1 P.V. Khadikar, B. Amma and M.A. Farooqui, Thermochim. Acta, 99 (1986) 109.
2 P.V. Khadikar, Acta. Chim., in press.

3 H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.
4 A.W. Coats and J.P. Redfern, Nature, 201 (1964) 68.
5 J. Shorter, Correlation Analysis in Organic Chemistry, Clarendon Press, Oxford, 1973.
6 B. Amma and P.V. Khadikar, Ph.D. Thesis, Vikram University, Ujjain, 1980.
7 A. Vogel, A Textbook of Quantitative Inorganic Analysis, Longmans, London, 1969.
8 D.W. Johnson and P.K. Gallagher, Thermochim. Acta, 5 (1973) 455.
9 S. Glasstone, Textbook of Physical Chemistry, Elsevier, New York, 2nd edn., 1963.
10 P.V. Khadikar, J. Thermal Anal., 32 (1987) 737.
11 P.V. Khadikar, J. Thermal Anal., 32 (1987) 748.
12 P.V. Khadikar and M.A. Farooqui, Thermochim. Acta, 96 (1985) 213.
13 P.V. Khadikar and M.G. Kanungo, J. Indian Chem. Soc., 52 (1975) 473.
14 P.V. Khadikar and M.A. Farooqui, J. Thermal Anal., 32 (1987) 729.
15 P.V. Khadikar and Nitin Sapre, Thermochim. Acta, 128 (1988) 55.
16 P.H. Fong and D.T.Y. Chen, Thermochim. Acta, 18 (1977) 273.
17 A. Sestak, V. Satava and W.W. Wendlandt, Thermochim. Acta, 7 (1973) 447.
18 T. Ozawa, H. Kambe and P.D. Garn (Eds.), Thermal Analysis, Wiley, New York, 1974.
19 S. Glasston and D. Lewis, Elements of Physical Chemistry, Macmillan, London, 2nd edn., 1960.
20 S. Glasstone, K.J. Laidler and H. Eyring, The Theory of Rate Processes, McGraw-Hill, New York, 1941.
21 O. Exner, Collect. Czech. Chem. Commun., 29 (1962) 1094.
22 S. Glasstone, Textbook of Physical Chemistry, Macmillan, Bombay, 2nd edn., 1974.
23 P.V. Khadikar, Thermochim. Acta, 127 (1988) 55.
24 P.V. Khadikar, Thermochim. Acta, 132 (1988) 25.
25 S.M. Ali, Ph.D. Thesis, D.A. University, Indore, 1987.
26 B.D. Heda, Ph.D. Thesis, Indore University, Indore, 1980.