Asian Journal of Chemistry Vol. 7, No. 4 (1995), 697–704

Thermal Behaviour of Pyridine Adducts of Metal Salicylhydroxamate: Depyridination of Oxovanadium (IV)-5-Bromo-Salicylhydroxamate-Pyridine

PADMAKAR V. KHADIKAR, TAGHI GHADERIAN, PADAM VIR SINGH RAJPUT, and JUGAL KISHORE AGRAWAL*
Chemical Laboratory, Shri G.S. Inst. of Tech. & Science
23, Park-Road, Indore-452 003, India

The TG-DTG-DTA analysis of mixed-ligand complex of oxovanadium(IV) with 5-bromo salicylhydroxamic acid (5-BSHA) and pyridine (PY) was investigated. The results have shown that mainly two step decomposition occurred wherein two pyridine moieties are lost in one single-step while 5-BSHA moieties are eliminated simultaneously, various kinetic and thermodynamic parameters for these steps were estimated employing Coats-Redfern and Horowitz-Metzger methods using computer program designed by us on ICIM-6,000 Main Frame.

INTRODUCTION

Salicylhydroxamic acid and nuclear substituted salicylhydroxamic acids play an extremely important role in the structure and function of a number of biological significant molecules generally by virtue of their being coordinated to a metal ion. Very few systems are reported in the literature showing their thermal stability and structure-activity-relationship. The thermal properties of the metal chelates of the parent salicylic acids have been reported earlier[1–5]. The renewed interest of the authors in salicylhydroxamic acid-metal chelates is due to their high stability, their effective use in chemical separations and their biological potential[6–10]. The present communication deals with the thermal behaviour of pyridine adducts of oxovanadium(IV) with 5-bromo-salicylhydroxamic acid-[VO(II)-(5-BSHA)$_2$-(PY)$_2$]. Various kinetic and thermodynamic parameters are estimated from TG and DTG data employing the method of Coats-Redfern and Horowtiz-Metzger[11, 12].

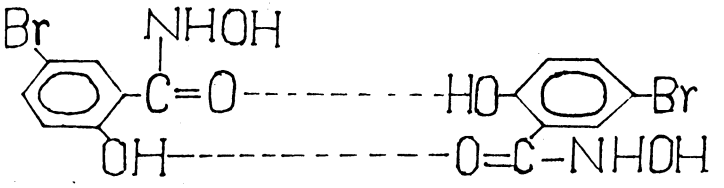
EXPERIMENTAL

TG-DTA-DTG were recorded employing Perkin-Elmer, Thermal Analyser at RSIC, Nagpur on 100 mg of the sample, in static air at a heating rate of 4°/min T4 chart speed was maintained at 3 in/hr. The sample was packed as uniformly as possible in platinum crucible of appropriate size. Each sample was homogenized by sieving below 100 mesh before packing. 5-BSHA as well as VO(II)-(5-BSHA)$_2$-(PY)$_2$] were prepared employing the method described earlier[13] and characterised by elemental analysis, UV and IR techniqes. Their purity was checked by TLC.

The IR spectra of 5-BSHA measured in KBr disc showed a peak at 965 cm^{-1}, 1575 cm^{-1}, 1620 and 1600 cm^{-1}, which can be assigned to NO_2, C=N and C=O respectively. A peak at 3,500 to 3,700 cm^{-1} corresponding to

the free —OH groups is not observed; instead a broad peak at 3,290 (S) cm^{-1} confirms the intramolecular hydrogen bonding of the two —OH groups. Based on the above observation, the following structure can be assigned to 5-BSHA.

The structure is in accordance with our X-ray diffraction[14] as well as thermal[15] studies on 5-BSHA.



Presentation of the data

DTA-TG-DTG trace recorded for [VO(II)-(5-BSHA)$_2$-(PY)$_2$] is presented in Fig. 1, while the data needed for the calculations of various parameters by Coats-Redfern [11] and Horowitz-Metzger [12] methods are presented in Figs. 2 and 3 respectively and also recorded in Table 2 and 3. Table-1 gives the thermal analysis of [VO(II)-(5-BSHA)$_2$-(PY)$_2$]. The various kinetic and thermodynamic parameters are recorded in Table-4.

RESULTS AND DISCUSSION

Thermal properties:

Fig. 1 shows that [VO(II)-(5-BSHA)$_2$-(PY)$_2$] is stable upto 12°C and then it starts decomposing apparently in two main steps. A close look at Fig. 1 indicates very weak TG-horizontals in between the temperature range 300–540°C, indicating simultaneous loss of 5-BSHA moieties. The observed weight loss during the temperature range 120–280°C indicates the loss of two pyridine moieties. It is

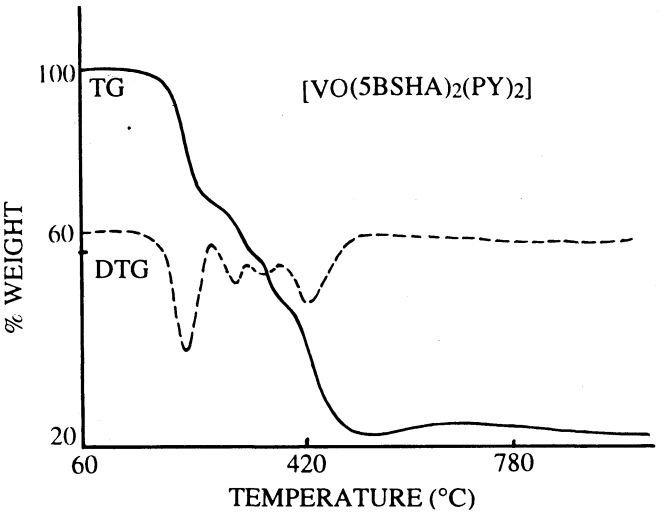


Fig. 1 (continued)

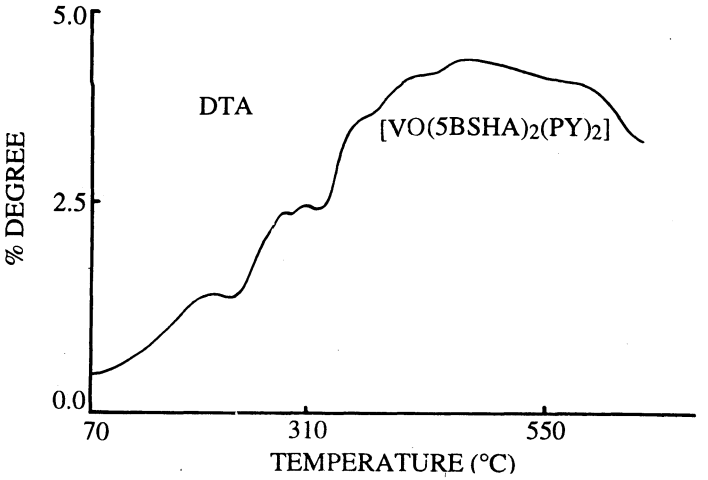


Fig. 1 TG-DTG-DTA traces for oxovanadium (IV)-5-bromosalicylhydroxamate-pyridine: VO-(5-BSHA)$_2$-(PY)$_2$

interesting to note that this is also the temperature range during which two water molecules are lost from [VO(II)-5-BSHA$_2$-2H$_2$O]. Thus, the bonding ability of the pyridine adduct is similar to that of water molecules. During the temperature-range 300–540°C both 5-BSHA moieties are lost simultaneously. The maximum thermal decomposition occures in the temperature range 340–390°C and the process is complete around 390–540°C. The thermal properties of [VO(II)-(5-BSHA-PY)$_2$] are presented in Table-1.

TABLE-1
THERMAL CHARACTERIZATION OF OXOVANADIUM (IV) MIXED-LIGAND COMPLEX OF 5-BROMOSALICYLHYDR OXAMIC ACID AND PYRIDINE

S.No.	TG Temp.-Range (°C)	Ts (°C)	DTG Range (°C) (Peak)	% Loss Found (Cal.)	Remark(s)
1.	120–280	230	120–295 (230)	25.4 (23.93)	Loss of two Pyridine -moieties
2.	300–540*	435	Multiple peaks*	52.43 (56.6)	Loss of two 5 BSHA-moieties
			295–370 (320)	75.94 —	
			390–540 (435)		

*Very small multiple TG-horizontals obtained are due to simultaneous depyridination and debromination of 5-BSHA as well as loss of 5-BSHA moieties during the thermal decomposition of VO(II)-5-BSHA>PY.

The residue from the thermogravimetric run of the compound was weighed and compared with the weight that would be obtained if the residue were a metal oxide. It was found that the percentage of metal found is less than the theoretical value. However, the sum percentage of metal and ligand from the thermogram equals the theoretical value. Hence, it can be concluded that during the process of decomposition some of the metal volatilizes and escapes along with ligand.

KINETIC AND THERMODYNAMIC PARAMETERS

(a) Order of reaction

The order of reaction (n) for the thermal decomposition of [VO(II)-(5-BSHA-PY)$_2$] was estimated using the following equation proposed by Horowitz and Metzger[12]:

$$C_s = n^{1/(1-n)}$$

where C_s is the weight function of the substances present at the DTG peak temperature Ts. 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_t^f = final weight and w_0 = initial weight of the substances. The order of the decomposition of [VO(II)-(5-BSHA-PY)$_2$] is obtained by comparing the C_s value yielded by the above method with the values given in the Horowitz-Metzger[12] table. The order was found to be one.

TABLE-2
COATS-REDFERN DATA FOR THE THERMAL DECOMPOSITION OF OXOVANADIUM MIXED-LIGAND CHELATE OF 5-BROMOSALICYLHYDROXAMIC ACID AND PYRIDINE

	S.No.	Temperature °C	α	$1/T \cdot 10^3$	$\log\left[-\ln\frac{(1-\alpha)}{T^2}\right]$
STEP-I	1.	223	0.192	4.484	–5.367
	2.	231	0.385	4.319	–5.043
	3.	240	0.480	4.166	–4.944
	4.	244	0.673	4.089	–4.728
	5.	253	0.769	3.953	–4.640
	6.	270	0.365	3.704	–4.560
STEP-II	7.	313	0.0361	3.195	–6.425
	8.	321	0.0963	3.110	–6.009
	9.	330	0.156	3.030	–5.807
	10.	343	0.180	2.915	–5.771
	11.	356	0.277	2.809	–5.592
	12.	368	0.337	2.714	–5.518
	13.	381	0.398	2.621	–5.458
	14.	394	0.458	2.535	–5.405
	15.	407	0.518	2.454	–5.357
	16.	416	0.578	2.404	–5.302
	17.	420	0.614	2.382	–5.267
	18.	433	0.722	2.309	–5.165
	19.	440	0.759	2.276	–5.156
	20.	446	0.380	2.242	–4.973
	21.	458	0.940	2.181	–4.874

(b) Kinetic parameters

Coats-Redfern[11] and Horowitz-Metzger[12] are the methods most widely used for the estimation of energy of activation E* and the pre-exponential factor A.

The expression used by Coats-Redfern[11] for this purpose is:

$$\log\left[\frac{AB}{\beta E^*}\left(1-\frac{2RT}{E^*}\right)\right]\frac{E^*}{2.3RT} = \begin{cases}\log\left[-\ln(1-\alpha)/T^2\right] & \text{for } n=1\\ \log\left[1-(1-\alpha)^{1-n/(1-n)t_2}\right] & \text{for } n\neq 1\end{cases}$$

where β = heating rate.

The treatment of Coats-Redfern method[11] of estimation E^* and A is presented in Table-2.

TABLE-3
HOROWITZ-METZGER DATA FOR THE THERMAL DECOMPOSITION OF OXOVANADIUM (IV)-MIXED-LIGAND CHELATES OF 5-BROMOSALICYL-HYDROXAMIC ACID AND PYRIDINE

S.No.	Temperature °C	θ	ln · ln (wt/wr)
STEP-I			
1.	223	-21.50	-1.544
2.	231	-13.00	-0.724
3.	240	- 4.500	-0.422
4.	244	- 0.000	+0.112
5.	253	8.500	+0.383
6.	270	25.50	+0.696
STEP-II			
7.	313	-103	-3.302
8.	321	-94.5	-2.289
9.	330	-86.0	-1.769
10.	343	-73.0	-1.613
11.	356	-60.0	-1.125
12.	368	-47.5	-0.888
13.	381	-34.5	-0.679
14.	394	-21.5	-0.491
15.	407	-08.5	-0.315
16.	416	00.0	-0.147
17.	420	04.0	-0.048
18.	433	17.0	+0.249
19.	440.5	24.0	+0.353
20.	446	30.0	+0.750
21.	458	42.5	+1.033

According to Horowitz-Metzger[12], the activation energy E^* and the pre-exponential factor A can be estimated using the following expressions:

$$E^*.0/2.3RTs^2 = \begin{cases} \log [-\ln (1-\alpha)], \text{ for } n = 1; \\ \log [1-(1-\alpha)^{1-n}/1-n], \text{ for } n \neq 1 \end{cases}$$

and

$$A = \begin{cases} \beta E^*/RTs^2 \exp (E^*/RTs) \text{ for } n = 0; \\ \beta E^*/RTs^2 C_s^{1-n} \exp (E^*/RTs) \text{ for } n \neq 0 \end{cases}$$

Here also β = heating rate.

The data needed for such calculation by the Horowitz-Metzger [12] method are recorded in Table 3.

(c) Thermodynamic parameters

The various thermodynamic parameters namely enthalpy of activation (H^*), free entry of activation (G^*), entropy of activation (S^*) and the specific rate constant K_γ are obtained from their mutual relationships:

$$S^* = (\log AhkT) \cdot R$$

where h and k are the Planck and Boltzmann constants respectively.

$$G^* = E^* - S^* \cdot Ts$$

$$H^* = E^* - R \cdot Ts$$

$$K_\gamma = A \cdot \exp (-E^*/RTs)$$

Regression Analysis

In order to obtain precise values for the above mentioned parameters, the data obtained in each of the two methods are subjected to the regression analysis—using the method of least squares. The values so obtained for the various kinetic and thermodynamic parameters are recorded in Table-4.

TABLE-4
REGRESSION ANALYSIS (LEAST SQUARE COMMAND) FOR THE THERMAL DECOMPOSITION OF OXOVANADIUM (IV) MIXED-LIGAND CHELATE OF 5-BROMOSALICYLHYDROXAMIC ACID AND PYRIDINE

S.No.	Parameters	Coats-Redfern		Horwitz-Metzger	
		Step-I	Step-II	Step-I	Step-II
1.	ΣX	24.717	63.888	-5.000	-415.5000
2.	ΣY	-29.283	-111.339	-1.499	-011.7810
3.	ΣX^2	102.198	206.054	13.740	44830.7500
4.	ΣY^2	143.362	594.564	3.727	30.3000
5.	$(\Sigma X)^2$	610.924	4081.715	25.000	172640.2500
6.	$(\Sigma Y)^2$	857.467	12396.395	2.246	138.7370
7.	ΣXY	-121.019	-337.142	65.482	1117.3000
8.	m	-1.183	-2.357	0.047	0.0239
9.	b	-0.007	2.423	0.158	0.1084
10.	R	0.999	0.988	0.939	0.9470

The values of correlation-coefficient of the order of 0.998 show an excellent applicability of these methods. The values of kinetic and thermodynamic parameters, obtained in general, agree well with an estimated uncertainty of +1.0 kcal/mole and are recorded in Table-5.

TABLE-5
KINETIC AND THERMODYNAMIC PARAMETERS FOR THERMAL DECOMPOSITION OF OXOVANADIUM(IV) MIXED-LIGAND COMPLEX OF 5-BROMOSALICYLHYDROXAMIC ACID AND PYRIDINE

S.No.	Step	TS (K)	Method b	E^*	log A	S^*	H^*	G^*	log Kr
1.	I	230	CR	5.41	4.51	-16.27	4.93	9.39	4.50
			HM	5.59	4.72	-15.86	5.11	9.47	4.70
			Mean	5.50	4.62	-16.06	5.02	9.43	4.60
2.	II	435	CR	10.93	7.23	-11.33	10.09	15.63	7.22
			HM	8.22	3.63	-18.48	7.40	15.91	3.62
			Mean	9.58	5.44	-14.91	8.74	15.77	5.42

[a] E^* = energy of activation, kcal $mole^{-1}$; A = pre-exponational factor, s^{-1}; H^* = enthalpy of activation, kcal. $mole^{-1}$, Kr = specific rate-constant, s^{-1}; S^* = entropy of activation, e.u.; G^* = free energy of activation, kcal $mole^{-1}$
[b] CR = Coats-Redfern method; HM = Horowitz-Metzger method.

The energy of actrivation E^* for the elimination of pyridine (step I) obtained by Coats-Redfern[11] as well as Horowitz-Metzger[12] methods agree well within the experimental limit., the average value being 5.5 kcal. The value is comparable to the usual values of the activation energies for dehydration of the hydrated salts[16]. The pyridine moieties in [VO(II)-(5-BSHA-PY)$_2$] appears, therefore, to be bonded in an analogous fashion as the water molecule in salt hydrates. The process of the depyridination of these complexes may thus be likened to the dehydration of salt hydrates and both processes take place at comparable temperature range too.

The energy of activation E^* for the loss of two 5-BSHA moieties as determined by the Horowitz-Metzger method is slightly less than the one calculated from the Coats-Redfern method. This may, probaby be due to the fact that 5-BSHA moieties are not lost in one single step. However, the value is comparable to those obtained for the thermal decomposition of similar ligand moieties, *viz.*, salicylic acid[1-5], salicylhydrazide[17] and salicylhydroxamic acid[18].

The other kinetic and thermodynamic parameters are also similar to the dehydration of the hydrated salts and the elimination of the other ligand moieties referred above.

The Thermochemical Reaction Scheme

Based on the above results the thermochemical reaction scheme for the thermal decomposition of [VO(II)-(5-BSHA)$_2$-(PY)$_2$] may be illustrated as follows:

Within the Temperature Range 120–280°C

During this temperature range depyridination of the chelate takes place. The reaction can be represented as under:

$$[VO\text{-}(5\text{-}BSHA)_2\text{-}(PY)_2] \xrightarrow{120\text{–}180^\circ C} VO\text{-}(5\text{-}BSHA)_2 + 2PY$$

where

5 BSHA = bromosalicylhydroxamic acid ligand and PY = pyridine.

Within the Temperature Range 300–540°C

Though the decomposition appears to be a two-step decomposition two very small inflections/TG horizontal are slightly observed at 295°–370°C and 390–540°C having DTG peak temperatures at 320 and 435°C respectively. This leads to the conclusion that the 5-BSHA moieties are lost in succession:

$$[VO\text{-}(5\text{-}BSHA)_2] \longrightarrow VO\text{-}(5\text{-}BSHA) + 5\text{-}BSHA$$

Volatile products (CO_1, CO_2, H_2O, Br_2, N_2, nitrogen oxide etc.)

$$[VO\text{-}(5\text{-}BSHA)] \longrightarrow V_2O_5$$

Volatile products as above

REFERENCES

1. P.V Khadikar, *Thermochim. Acta*, **127**, 37 (1988).
2. B.D. Heda and P.V. Khadikar, *Thermochim. Acta*, **41**, 25 (1980).
3. P.V. Khadikar, S.M. Ali and B.D. Heda, *J. Thermal Anal.*, **30**, 305 (1985).
4. _____, *J. Thermal Anal,*. **30**, 167 (1985).
5. B.D. Heda and P.V. Khadikar, *Bull. Soc. Chim. Belg.*, **89**, 1 (1980).
6. S.N. Kane, A. Gupta, S.M Ali and P.V. Khadikar, *Hyo. Int.*, **35**, 927 (1987)
7. P.V. Khadikar, M.M. Mangelson and S.P. Pandharkar, *Jap. J. Appl. Phys.*, **28**, 709 (1989).
8. P.V. Khadikar and S.P. Pandharkar, *Physica B*, **158**, 227 (1959).
9. P.V. Khadikar, B. Pol and S.M. Ali, *Spectrochim. Acta*, **42A**, 7355 (1980).
10. P.V. Khadikar and S.P. Pandharkar, *Thermochim. Acta*, **99**, 119 (1988).
11. A.W. Coats and J.P. Redfern, *Nature*, **201**, 68 (1964).
12. H. Horowitz and G.Metzger, *Anal. Chem.*, **35**, 1464 (1963).
13. S.N. Kane, A. Gupta, S.M. Ali and P.V. Khadikar, *Hyp. Int.* (in press).
14. N.K. Dalley and P.V. Khadikar, unpublished results on X-ray diffraction, Brigham Young Univ. Prov. Utah (USA) (1988).
15. P.V. Khadikar, S.M. Ali and Nitin S. Sapre, *J. Thermal Anal.* (under publication).
16. W.W. Wendndlandt, Thermal Analysis, 3rd edn., John Wiley, N.Y. (1986)
17. P.V. Khadikar, T. Gadherian, P. Suri and Nitin S. Sapre, *Thermochim. Acta*, **157**, 203 (1990).
18. P.V. Khadikar, *Thermochim. Acta*, **132**, 25 (1988).

(*Received*: 8 October 1994; *Accepted*: 3 February 1995). AJC-941