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THERMAL DECOMPOSITION KINETICS OF VANILLIDENE ANTHRANILIC ACID COMPLEXES OF COBALT(II), NICKEL(II), COPPER(II) AND ZINC(II)

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The thermal decomposition of cobalt(II), nickel(II), copper(II) and zinc(II) complexes of the Schiff base vanillidene anthranilic acid was studied by TG. The chelates show somewhat similar TG plots when heated in an atmosphere of air. Thermoanalytical data (TG and DTG) of these chelates are presented in this communication. Interpretation and mathematical analysis of these data and evaluation of order of reaction, the energy and entropy of activation based on the differential method employing the Freeman–Carroll equation, the integral method using Coats–Redfern equation and the approximation method using the Horowitz–Metzger equation are also given. On the basis of experimental findings in the present course of studies, it is concluded that the relative thermal stability of vanillidene anthranilic acid chelates can be aligned as Co(II) $\cong$ Ni(II) $>$ Zn(II) $>$ Cu(II).

Very few systems are reported showing the relationship between thermal stability of metal chelates and structure of chelating agents [1]. Wendlandt [2–5] and Hill [6, 7] studied the thermal properties of metal chelates with different types of complexing ligands. A study of thermal decomposition of Schiff base complexes of nickel and cobalt has been reported by Bhaskare and More [8]. Recently Lehtinen and Maire have made a report of the thermal stability and kinetics of Cu(II) and Ni(II) chelates of the Schiff bases derived from 5-bromosalicylaldehyde and some medicinal sulfonamides [9]. Thermogravimetry of some noble and common metal chelates of 5-amino 1,3,4-thiadiazole-2 thiol and N-acetylacetone anthranilic acid was investigated by Johri and Arora [10].

The purpose of this study is to report the thermal stability of the metal chelates and also to calculate the kinetic parameters viz., energy of activation, entropy and order of reaction which corresponds to the decomposition of the complex.

Experimental

The metal complexes of vanillidene anthranilic acid ($C_{15}H_{13}O_4N$) were prepared by refluxing 1M aqueous solution of the metal chloride and 1M methanolic solution of the ligand for about half an hour on a water bath. The precipitates were filtered, washed with aqueous methanol and dried in vacuum desiccator. The structures of these chelates were found [11] to be of the general formula $[ML(H_2O)]_2$ where M = Co(II), Ni(II), Cu(II), Zn(II) and LH_2 = vanillidene anthranilic acid.

Apparatus

A Stanton recording thermobalance Model TR-1 was used for recording TG traces. The heating rate was 4 K min^{-1} and chart speed was 6 in. h^{-1}. The atmosphere was static air. The samples were taken in tall narrow crucibles to avoid loss by spattering.

Treatment of data

The instrumental TG traces were re-drawn as the mass *vs.* temperature (TG) curves and also as the rate of loss of mass *vs.* temperature (DTG) curves. The curves were drawn using standard curve sets. TG, DTG traces of all these chelates are presented in Fig. 1.

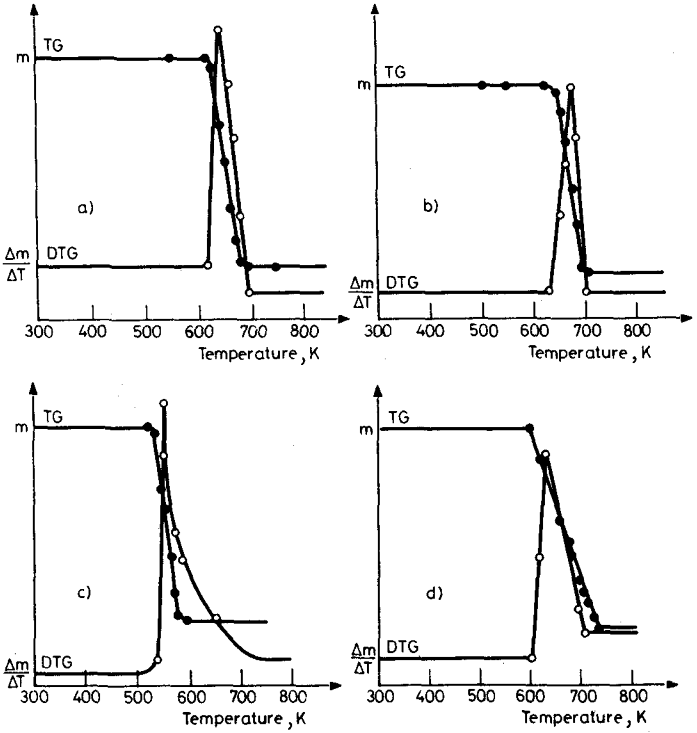

Fig. 1 TG and DTG traces. $a = [CoL(H_2O)]_2$, $b = [NiL(H_2O)]_2$, $c = [CuL(H_2O)]_2$, $d = [ZnL(H_2O)]_2$

The TG curves were studied in greater detail. All the TG curves were essentially of the same pattern. Three different methods were used to evaluate kinetic data from these TG traces.

The differential method using Freeman–Carroll equation [12]

The Freeman–Carroll equation was used in the form

$$\frac{\Delta \log \frac{dw}{dt}}{\Delta \log w_r} = \frac{-\frac{E^*}{2.303\,R}\Delta(T^{-1})}{\Delta \log w_r} + n \tag{1}$$

where $w_r = w_\infty - w$; w_∞ = mass loss at the completion of the reaction; w = mass loss up to time t; T = absolute temperature at time t; n = order of reaction; R = gas constant in cal and E^* = energy of activation in J mol^{-1}. Of the above terms, w_r and T can be directly obtained from the TG traces. The mass temperature gradient (dw/dT) could be obtained by drawing tengents, but a more accurate method, based in Stirling's central difference formula for six points [13] was employed. The temperature slopes, dw/dT, were converted into time slopes, dw/dt, using the relation,

$$\frac{dw}{dt} = \frac{dw}{dT}\,\frac{dT}{dt} = \left(\frac{dw}{dT}\right)\varphi \tag{2}$$

where φ is the heating rate.

A plot of

$$\frac{\Delta(T^{-1})}{\Delta \log w_r} \quad \text{versus} \quad \frac{\Delta \log \frac{dw}{dt}}{\Delta \log w_r}$$

was drawn and was found to be linear from which the order of reaction and activation energy were obtained. The order of reaction (n) was found to be almost unity. The usual first-order rate law expression,

$$\frac{dx}{dt} = k(a-x) \tag{3}$$

can be put in the following form using the terms w and w_r

$$\frac{dw}{dt} = kw_r \tag{4}$$

combining this with Arrhenius equation i.e.,

$$k = Z \exp\left(-\frac{E^*}{RT}\right) \tag{5}$$

we get

$$\log\left[\frac{\frac{dw}{dt}}{w_r}\right] = -\frac{E^*}{2.303\,RT} + \log Z \tag{6}$$

A plot of the left hand side expression against (T^{-1}) was found to be linear, from the slope of which E^* was calculated. Z was calculated from the intercept and entropy of activation, ΔS^* was obtained from the equation

$$Z = \frac{kT_s}{h} \exp\left(\frac{\Delta S^*}{R}\right) \tag{7}$$

where k is the Boltzmann constant and h is the Planck constant and T_s is the peak temp. from DTG. Typical curves concerning the application of the Freeman–Carroll equation ($n = 1$) to all the chelates are given in Fig. 2.

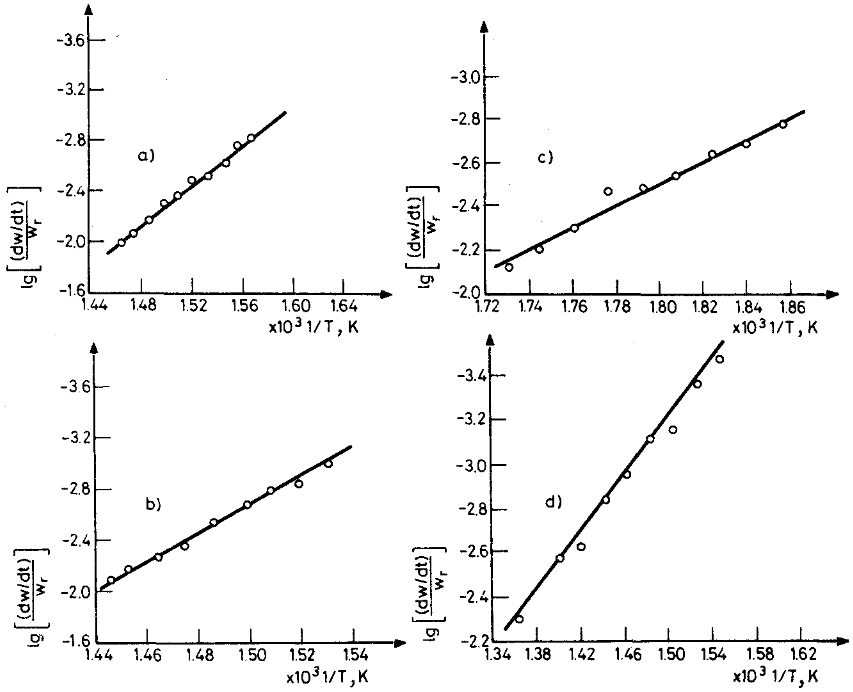

Fig. 2 Freeman–Carroll plot. $a = [\mathrm{CoL(H_2O)}]_2$, $b = [\mathrm{NiL(H_2O)}]_2$, $c = [\mathrm{CuL(H_2O)}]_2$, $d = [\mathrm{ZnL(H_2O)}]_2$

The integral method using the Coats–Redfern equation [14]

For first order processes Coats–Redfern equation may be written in the form

$$\log\left[\frac{\ln \frac{W_\infty}{W_\infty - W}}{T^2}\right] = \log\left[\frac{ZR}{\varphi E}\left(1 - \frac{2RT}{E^*}\right)\right] - \frac{E^*}{2.303\,RT} \tag{8}$$

since $1 - 2RT/E^* \approx 1$, a plot of L.H.S. against $1/T$ was drawn (Fig. 3). E^* was calculated from the slope and Z was found out from the intercept.

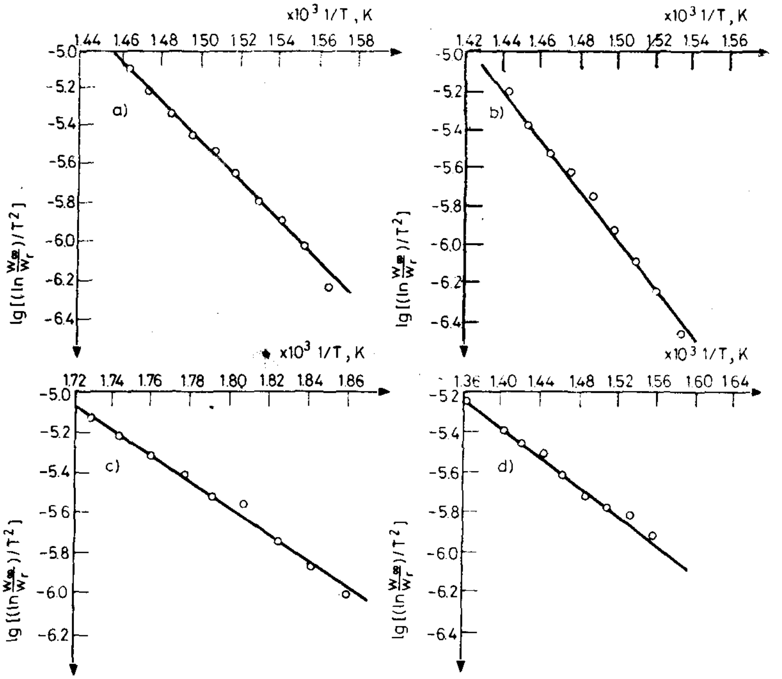

Fig. 3 Coats–Redfern plot. $a = [CoL(H_2O)]_2$, $b = [NiL(H_2O)]_2$, $c = [CuL(H_2O)]_2$, $d = [ZnL(H_2O)]_2$

The approximation method using the Horowitz–Metzger equation [15]

The Horowitz–Metzger equation applicable to first order kinetic processes is in the form

$$\log\log\frac{W_\infty}{W_r} = \frac{E^*\Theta}{2.303\,RT_s^2} - \log 2.303 \tag{9}$$

where $\Theta = T - T_s$ and the other terms are as described earlier. A plot of log log (W_∞/W_r) vs Θ was drawn and was found to be linear; from the slope of which E^* was calculated. Typical curves are given in Fig. 4. The pre-exponential factor Z was calculated from the equation

$$\frac{E^*}{RT_s^2} = \frac{Z}{\varphi \exp\left(-\frac{E^*}{RT_s}\right)} \tag{10}$$

The entropy of activation ΔS^* was calculated from the equation used earlier for the purpose.

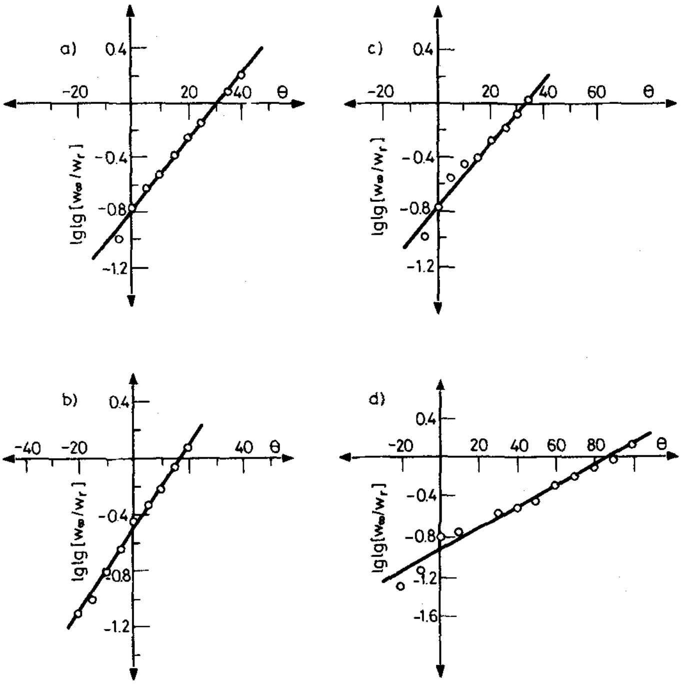

Fig. 4 Horowitz–Metzger plot. $a = [CoL(H_2O)]_2$, $b = [NiL(H_2O)]_2$, $c = [CuL(H_2O)]_2$ $d = [ZnL(H_2O)]_2$

Results and discussion

The decomposition temperature ranges for the metal chelates are given in Table 1. Data from independent pyrolytic experiments (carried out by heating weighed samples taken in porcelain crucibles in an atmosphere of air) are also included in Table 1. Kinetic parameters calculated by employing the Freeman–Carroll, the Coats–Redfern and Horowitz–Metzger equations are summarized in Table 2. The overall loss of mass from the TG curve is 80% for $[CoL(H_2O)]_2$, 80% for $[NiL(H_2O)]_2$, 74% for $[CuL(H_2O)]_2$ and 78% for $[ZnL(H_2O)]_2$ while the calculated loss in mass for these conversions are

$3[CoL(H_2O)]_2 \longrightarrow 2\ Co_3O_4$	76.85%
$[NiL(H_2O)]_2 \longrightarrow 2\ NiO$	78.40%
$[CuL(H_2O)]_2 \longrightarrow 2\ CuO$	77.32%
$[ZnL(H_2O)]_2 \longrightarrow 2\ ZnO$	76.91%

Table 1 Thermal decomposition data

Substance	Decomposition temp. range, K	% mass loss			Peak temp. from DTG, K	Order of reaction	
		Observed from TG	From independent pyrolysis	Calculated		Freeman–Carroll method	Zsakó's modified Doyle method
$[CoL(H_2O)]_2$	633–693	80	77.02	76.85	643	1.05	1
$[NiL(H_2O)]_2$	633–703	80	78.20	78.40	673	1.10	1
$[CuL(H_2O)]_2$	533–583	74	77.80	77.32	543	1.16	1
$[ZnL(H_2O)]_2$	603–733	78	78.04	76.91	623	0.98	1

LH_2 = vanillidene anthranilic acid

Table 2 Kinetic data

Substance	Parameters	From Freeman–Carroll equation	From Coats–Redfern equation	From Horowitz–Metzger equation
$[CoL(H_2O)]_2$	E^* kJ mol^{-1}	174.14	191.55	186.35
$m = 50$ mg	Z s^{-1}	2.39×10^{11}	5.20×10^{12}	4.87×10^{12}
$w = 40$ mg	ΔS JK^{-1} mol^{-1}	-33.49	-7.88	-8.43
$[NiL(H_2O)]_2$	E^* kJ mol^{-1}	201.51	201.51	197.18
$m = 45$ mg	Z s^{-1}	1.23×10^{13}	1.24×10^{13}	6.89×10^{12}
$w = 36$ mg	ΔS JK^{-1} mol^{-1}	-1.09	-0.25	-5.92
$[CuL(H_2O)]_2$	E^* kJ mol^{-1}	119.72	127.67	129.10
$m = 50$ mg	Z s^{-1}	6.47×10^{8}	2.58×10^{9}	9.05×10^{9}
$w = 37$ mg	ΔS JK^{-1} mol^{-1}	-81.28	-69.77	-59.33
$[ZnL(H_2O)]_2$	E^* kJ mol^{-1}	119.72	79.83	82.59
$m = 50$ mg	Z s^{-1}	1.64×10^{8}	3.89×10^{3}	1.43×10^{4}
$w = 39$ mg	ΔS JK^{-1} mol^{-1}	-93.8	-182.43	-171.58

The end products are confirmed to be Co_3O_4, NiO, CuO and ZnO from their X-ray diffraction pattern.

The loss of coordinated water and the ligand is found to be in one step. According to Nikolaev et al. [16] water eliminated below 150° can be considered as the water of crystallization and water eliminated above 150° may be due to its coordination to the metal ion. In the present studies it is observed that the decomposition starts only after 250°. So the water present is the coordinated water. Initial decomposition temperature and inflection temperature have been used to determine thermal stability of metal chelates. The initial decomposition temperature is frequently used to define the relative thermal stability of metal chelates [16]. On the basis of experimental findings in the present course of studies and the observations made by earlier workers

[17, 18], the relative thermal stability of vanillidene anthranilic acid chelates can be given as

$$\text{Co(II)} \cong \text{Ni(II)} > \text{Zn(II)} > \text{Cu(II)}$$

Decomposition kinetics

The analysis of data using the Freeman—Carroll equation and Zsakó's modified Doyle method [20, 21] by calculation of standard deviation gives the order of the decomposition reaction near unity in all these cases (Table 1). Based on this value of the order of reaction, the kinetic parameters are evaluated.

The values of energy of activation E^* obtained for Co(II) complex are 174.14, 191.55 and 186.35 kJ mol^{-1} by the three methods respectively while for Ni(II) complex the values are 201.51, 201.51 and 197.18 kJ mol^{-1} and for Cu(II) complex the values are 119.72, 127.67 and 129.10 kJ mol^{-1} and for Zn(II) complex the values are 119.72, 79.83 and 82.59 kJ mol^{-1}. The entropies of activation vary from -182.43 to -0.25 JK^{-1} mol^{-1}. The negative values of ΔS^* in these complexes indicate that the activated complex has a more ordered structure than the reactants and that the reactions are "slower than normal" [22].

The kinetic parameters show a somewhat different trend from that of thermal stability. This is not surprising, because the decisive criteria in kinetics are often quite different from those which decide thermal stability. It is seen that E^* values and Z values increase in the order

$$[\text{ZnL}(\text{H}_2\text{O})]_2 < [\text{CuL}(\text{H}_2\text{O})]_2 < [\text{CoL}(\text{H}_2\text{O})]_2 < [\text{NiL}(\text{H}_2\text{O})]_2$$

* * *

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References

1 W. W. Wendlandt, Anal. Chim. Acta, 17 (1957) 428.
2 G. D. Ascenzo and W. W. Wendlandt, J. Thermal Anal., 1 (1969) 423.
3 G. D. Ascenzo and W. W. Wendlandt, Anal. chim. Acta, 50 (1970) 79.
4 F. C. Chang and W. W. Wendlandt, Thermochim Acta, 2 (1971) 293.
5 D. L. Perry, C. Vaz and W. W. Wendlandt, Thermochim. Acta, 9 (1974) 76.
6 C. G. Scency, J. O. Hill and R. J. Magee, Thermochim. Acta, 11 (1975) 301.
7 C. G. Scency, J. F. Smith, J. O. Hill and R. J. Magee, J. Thermal Anal., 9 (1976) 415.
8 C. K. Bhaskare, P. G. More and P. P. Hankare, Proceedings of the National Symposium on Thermal Analysis, 1981.
9 Lehtinen and Maire, Acta Pharm., Fenn., 90 (1981) 187.
10 K. N. Johri and B. S. Arora, Thermochim. Acta, 54 (1982) 237.
11 J. Chacko and G. Parameswaran, J. Ind. Chem. Soc. (communicated).
12 E. S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
13 W. E. Milne, Numerical Calculus, Princeton University Press, Princeton, New Jersey, 1949, 99.
14 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
15 H. H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.
16 A. V. Nikolaev, V. A. Logvinenko and L. I. Myachina, Thermal Analysis, Academic Press, New York, 1969, 779.
17 V. Sheshagiri, S. Rao and Brahmji, Z. Anal. Chem., 262 (1972) 275.
18 R. Sheshadri Naidu and R. Raghava Naidu, Ind. J. Chem., 15A (1977) 652.
19 J. Šestak, Talanta, 13 (1966) 567.
20 C. D. Doyle, J. Appl. Polym. Sci., 5 (1961) 285.
21 J. Zsakó, J. Phys. Chem., 72 (1968) 2406.
22 A. A. Frost and R. G. Pearson, Kinetics and Mechanism, John Wiley and Sons, New York, 1961.

Zusammenfassung — Die thermische Zersetzung von Cobalt(II)-, Nickel(II)-, Kupfer(II)- und Zink(II)-Komplexen der Schiffschen Base Vanillidenanthranilsäure wurde thermogravimetrisch untersucht. Die Chelate zeigen in einer Luftatmosphäre ähnliche TG-Kurven. Thermoanalytische Daten (TG and DTG) dieser Chelate werden mitgeteilt, interpretiert und mathematisch analysiert. Ebenfalls werden die Reaktionsordnung und die Energie und Entropie der Aktivierung nach der von Freeman—Carroll angewandten differentiellen Methode, nach der auf der Coats—Redfern-Gleichung basierenden integralen Methode und nach der die Horowitz—Metzger Gleichung benutzenden Näherungsmethode bestimmt. Aus den Befunden wird geschlossen, dass die thermische Stabilität von Vanillidenanthranilsäure-Chelaten in der Reihenfolge Co(II) $\cong$ Ni(II) $>$ Zn(II) $>$ $>$ Cu(II) abnimmt.

Резюме — Методом ТГ изучено термическое разложение комплексов двухвалентных кобальта, никеля, меди и цинка с шиффовым основанием ванилиденантраниловой кислотой. ТГ и ДТА-данные этих хелатов в атмосфере воздуха до некоторой степени были подобны. Представлена интерпретация и математический анализ полученных данных, а также определены порядок реакции, энергия и энтропия активации дифференциальным методом с использованием уравнения Фримена-Кэрролла, интегральным методом, используя уравнение Коутса—Рэдферна и методом приближений с использованием уравнения Хоровица—Мецгера. На основании полученных экспериментальных данных установлено, что относительная термоустойчивость хелатов может быть расположена в ряд Co $\cong$ Ni $>$ Zn $>$ Cu.