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NOTE

Kinetic Parameters of Copper(II) Complex of N-Hydroxy-N-(2-chloro-3-methyl)phenyl-N'-(2,6-dimethyl)-phenylbenzamidine Hydrochloride

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N-Hydroxy-N-(2-chloro-3-methyl)phenyl-N'-(2,6-dimethyl)phenylbenzamidine hydrochloride reacts with copper(II) to form water insoluble buff colored precipitate. The reaction is quantitative in the pH range 2.5-10.0. The thermal gravimetric analysis of the solid dry complex was done. The complex melts at 220 °C with decomposition. The decomposition takes place almost in one step in the range 220-500 °C. TGA data of decomposition has been used for the calculation of kinetic parameters *i.e.* energy of activation, frequency factor and entropy employing Coats-Redfern, Sharp-Wentworth, Piloyan-Novikova methods. The values obtained are in good agreement. The negative value of entropy suggests more ordered structure than free ligand.

Key Words: Kinetic parameters, N-Hydroxyamidine, Thermogravimetric analysis, Copper(II) complex.

Copper complexes of N-hydroxyamidines have been the subject of intense investigation due to their importance in biological, industrial and agricultural fields. Much work has been done on their synthesis and analytical application[1-5] but no reports are available on the solid state kinetic studies of such complexes.

Thermogravimetric analysis is a non-isothermal method, which is useful because a single experimental curve is sufficient to obtain an estimate of energy of activation, frequency factor and entropy and that the kinetic can be probed over an entire temperature range in a continuous manner without any gap. In present communication kinetic parameters of the copper complex of N-hydroxy-N-(2-chloro-3-methyl)phenyl-N'-(2,6-dimethyl)-phenylbenzamidine hydrochloride was calculated employing Coats-Redfern, Sharp-Wentworth and Piloyan-Novikova methods.

All the chemicals used were of AR grade. The copper complex of N-hydroxy-N-(2-chloro-3-methyl)phenyl-N'-(2,6-dimethyl)phenyl-benzamidine hydrochloride (m.p. 220 °C) has been prepared by adding

1 % solution of ligand in alcohol to copper sulphate solution drop wise with stirring till buff precipitate was obtained. The reagent was added in some excess for complete precipitation and solution was digested over boiling water bath for 20-30 min. The buff precipitate obtained was filtered, washed with 40 % alcohol then with water and dried.

The IR spectra was recorded in Perkin-Elmer spectrophotometer using KBr pellets and thermal analysis was carried out using heating rate 10 °C min^{-1} in Mettler Toledo instrument.

Elemental analysis data of copper(II) complex of N-hydroxy-N-(2-chloro-3-methyl)phenyl-N'-(2,6-dimethyl)phenylbenzamidine hydrochloride were found (calcd.) (%): C 66.78 (66.80), H 5.05 (5.2), N 7.08 (6.88), Cu 8.04 (8.1).

IR Spectra: A broad band at 2250 cm^{-1} in the spectra of ligand confirming the presence of azomethine nitrogen in hydroxyamidine[6] is absent in the IR spectra of copper complex indicating deprotonation of azomethine nitrogen. A strong band at 1610 cm^{-1} is observed in the spectra of free ligand which is due to -C=NH^+ which appears at 1585 cm^{-1} in the spectra of copper complex. This band shift to lower frequency by 25 cm^{-1} on complexation due to reduction of electron density in the azomethine linkage. The formation of -C=N---Cu coordinate bond[7] is confirmed. The (N-O) stretching mode appears at 970 cm^{-1} in copper complex supporting (N-O-Cu) bond in the complex. The metal ligand (Cu-N) band observed at 467 cm^{-1}.

The comparison of the spectra of free ligand and copper complex suggests that the band due to NH^+ stretching disappears while band due to C=N, N-O shifts on chelation with copper.

Thermal decomposition of copper complex and kinetic parameters: A careful analysis of thermo gravimetric curve shows the initial decomposition at 220 °C indicating the absence of water molecule in the coordination sphere of the metal[8]. It was confirmed by the absence of a peak around 3500 cm^{-1} in the IR spectra of the complex. The initial decomposition temperature is frequently used to define the thermal stability of the metal chelates. The complex is found to decompose almost in one step. The intermediates formed during decomposition usually undergo further decomposition without showing stability over a considerable range of temperature. The weight of ultimate pyrolysis product corresponds to metal oxide (10.06/10.32 %).

The kinetic parameters of the complex are evaluated employing Coats-Redfern, Sharp-Wentworth and Piloyan-Novikova methods.

Coats-Redfern method[9]: The equation for first order (n = 1) reaction is given by

$$\log[-\log(1-\alpha)/T^2] = \log AR/\beta E[1-2RT/E] - E/2.303RT$$

The graph between log [-log (1-α)/T^2] and 1000/T gave a straight line over a long range of a values.

Piloyan-Novikova method[10]: The equation for first order reaction is given by

$$\log [\alpha/T^2] = \log AR/\beta E - E/2.303RT$$

The graph between log [α/T^2] and 1000/T gave a straight line over a long range of a values.

Sharp-Wentworth method[11]: The equation for first order reaction is given by

$$\log [(dc/dt)/(1-c)] = \log A/\beta - E/2.303RT$$

A linear plot was obtained when a graph between log [(dc/dt)/(1-c)] and 1000/T was plotted.

The activation energy and frequency factor was calculated from slope and intercept respectively in each case.

Apparent entropy: The entropy has been calculated by Zsako[12] method. The value of ΔS is given by expression

$$\Delta S = 2.303 \log [Ah/kT_{½}]$$

The result obtained is given below:

Compound	Method	E_a (KJ mol^{-1})	A (s^{-1})	ΔS (JK^{-1} mol^{-1})
N-Hydroxy-N-(2-chloro-3-methyl)phenyl-N-(2,6-dimethyl)phenyl-benzamidine copper chelate	C-R	76.5886	2.1553×10^{-2}	-33.9543
	P-N	74.4613	2.6461×10^{-2}	-33.7491
	S-W	70.2068	3.2389×10^{-2}	-33.5467

REFERENCES

1. K. Satyanarayana and R.K. Mishra, *Anal. Chem.*, **46**, 1609 (1974).
2. H. Mohabey and R.K. Mishra, *J. Indian Chem. Soc.*, **57**, 142 (1980).
3. H. Mohabey, P.K. Sharma and R.K. Sharma, *Curr. Sci. (India)*, **50**, 1070 (1981).
4. S. Khan and H. Mohabey, *Asian J. Chem.*, **10**, 1035 (1998).
5. S.C. Tiwari and H. Mohabey, *Asian J. Chem.*, **17**, 2565 (2005).
6. A.D. Cross, An Introduction to Practical Infrared Spectroscopy, Academic Press, New York, p. 71 (1963).
7. J.R. Ferraro, Low Frequency Vibration of Inorganic and Coordination Compounds, Plenum Press, New York (1971).
8. W.W. Wendlandt and J.P. Smith, The Thermal Properties of Transition Metal Ammine Complexes, Elsevier, Amsterdam (1967).
9. A.W. Coats and J.P. Redfern, *Nature*, **201**, 68 (1964).
10. G.O. Piloyan and O.S. Novikova, *Russ. J. Inorg. Chem.*, **12**, 313 (1969).
11. J.H. Sharp and S.A. Wentworth, *Anal. Chem.*, **41**, 2060 (1969).
12. J. Zsako, *J. Phys. Chem.*, **72**, 2406 (1968).

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