October, 1972] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3073—3075(1972) 3073

Formation Constants of Some Bivalent Metal Chelates of *N*-Phenylbutyrohydroxamic Acid

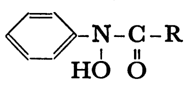
J. P. Shukla* and S. G. Tandon

Department of Chemistry, Government College of Science, Raipur, M.P., India

(Received December 25, 1970)

The formation constants for the metal chelates of Mn(II), Ni(II), Zn(II), and Cu(II) with *N*-phenylbutyrohydroxamic acid have been determined in 50 volume per cent dioxane-water mixture following the Bjerrum-Calvin pH titration technique and maintaining the titration medium at a constant salt background (0.1 M $KClO_4$) and a temperature 25±0.1°C. The formation constants found are $\log K_1=9.68$(Cu), 6.85(Zn), 6.67(Ni), 5.25(Mn), and $\log K_2=8.58$(Cu), 5.52(Zn), 5.21(Ni), and 4.09(Mn), the stability order being Mn<Ni<Cu>Zn.

Substitution of different groups at different positions of aryl nuclei of the parent compound influences the stabilities of the resulting metal complexes. A more or less quantitative survey of the effects of substitution in the aryl nuclei on the stability constants of metal chelates of the ligand was first carried out by Calvin and Wilson.[1] Such studies are important in as much as they help predict what type of substituents in the molecule might enhance its use for a particular purpose. Several *N*-arylhydroxamic acids represented by the general formula have been synthesised during the last



few years and their possible analytical applications examined. Recently, the stabilities of metal chelates of some aryl substituted *N*-arylhydroxamic acids (R=aryl), mainly of *N*-phenylbenzohydroxamic acid (PBHA) have been reported.[2,3] But so far no attempt seems to have been made except for a few instances[2,4] to elucidate the stability of metal chelates of alkyl substituted *N*-arylhydroxamic acids (R=alkyl). The present paper deals with the determination of formation constant of Cu(II), Ni(II), Zn(II), and Mn(II) chelates with *N*-phenylbutyrohydroxamic acid, P(n)BHA, by employing Calvin and Melchior's method,[5] commonly referred to as Bjerrum-Calvin pH titration technique. Titrations were carried out in duplicate in a medium of salt background 0.1 M adjusted with $KClO_4$, at 25±0.1°C. A ratio 10: 1 of the ligand to metal ion concentration was used in order to satisfy the highest possible coordination number namely, 6, of the metal ions under study. Since evaluation of the formation constant required knowledge of the acid dissociation constant not found in literature, it was also determined under similar experimental conditions. As both the ligand and its complexes are fairly insoluble in water, 1: 1 dioxane-water was used as the solvent medium.

Experimental

B.D.H. *p*-dioxane was purified by the procedure of Weissberger and Proskauer.[6] Carbonate free KOH was prepared following the method of Vogel[7] and diluted to 0.1 M; the proportion of dioxane and water in the final solution was 1: 1. It was standardized against analytical grade potassium hydrogen phthalate.

Measurements of pH were made with a Radiometer pHM-4c pH meter, saturated calomel reference electrode and a glass electrode. Buffer solutions of pH 4.01 (at 25°C) and 9.18 (at 25°C), prepared from potassium hydrogen phthalate and borax respectively, were used for standardization of the pH meter, which was done at the beginning of each titration and checked after completion.

Chelating Agent. P(n)BHA was synthesised by the method of Priyadarshini and Tandon.[8] This was recrystallised before use from a mixture of benzene and petroleum ether and dried in a vacuum over P_2O_5. Purity of the compound was checked by elemental analyses, mp, UV and IR spectra.

Metal Perchlorates. Metal salt solutions were prepared by dissolving the respective metal carbonates or oxides in a known volume of perchloric acid. The concentration of the metal ion in each of the metal perchlorates was determined by EDTA titration.[9] Finally, these solutions were suitably diluted before use. In the case of copper perchlorate, however, no further dilution of the stock solution was made since the pH of hydrolysis for Cu(II) is rather low, *i.e.* 5.3.[10]

Determination of Acid Dissociation Constant (pK_a). The titration procedure for determination of pK_a was essentially the same as that given by Albert and Serjeant.[11] A half millimoles of the compound was transferred to a four-necked, flat bottomed titration cell and dissolved in known volumes of dioxane and water. Five milliliters of 1 M $KClO_4$ was added to maintain a constant salt background of 0.1 M. The total volume of the contents was made to 47.5 m*l* by adding dioxane and water in such proportion that it finally became 1: 1 dioxane-water mixture. Before performing the titration

---

* Present address: Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay-85, India.

1) M. Calvin and K. W. Wilson, *J. Amer. Chem. Soc.*, **67**, 2203 (1945)

2) N. K. Dutt and T. Seshadri, *J. Inorg. Nucl. Chem.*, **31**, 2153 (1969).

3) G. A. Brydon and D. E. Ryan, *Anal. Chim. Acta*, **35**, 190 (1966).

4) J. P. C. Jaimini and N. C. Sogani, *J. Indian Chem. Soc.*, **45**, 59 (1968).

5) M. Calvin and N. C. Melchior, *J. Amer. Chem. Soc.*, **70**, 3270 (1948).

6) A. Weissberger and E. S. Proskauer, "Organic Solvents," Interscience Publishers, New York, Vol. 7, p. 139 (1955).

7) A. I. Vogal, "A Text Book of Quantitative Inorganic Analysis," 3 rd ed., Longmans (1961), p. 240.

8) U. Priyadarshini and S. G. Tandon, *J. Chem. and Eng. Data*, **12**, 143 (1967).

9) F. J. Welcher, "The Analytical Uses of Ethylenediamine tetraacetic Acid," D. Van Nostrand Co., Princeton (1961), p. 234.

10) H. T. S. Britton, "Hydrogen Ions," Vol. II, Chapman & Hall Ltd., London (1956), p. 102

11) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Methuen and Co, Ltd., London (1962), p. 28.

TABLE 1. DETERMINATION OF THE ACID DISSOCIATION CONSTANT

Concentration of P(n)BHA=0.01M at 50 m*l* level
Salt background=0.1M $KClO_4$
Medium=1:1 Dioxane-water
Temperature=25±0.1°C

Titrant 0.1M KOH (m*l*)	pH	Stoichiometric concentrations (10^{-3})		$[OH^-]$ (10^{-6})	$\frac{[HA]+[OH^-]}{[A^-]-[OH^-]}$	log of column 6	pK_a= (pH+column 7)
		[HA]	$[A^-]$				
0.05	10.200	9	1	1	9001/999	+0.955	11.155
1.00	10.570	8	2	3	8003/1997	+0.603	11.173
1.50	10.770	7	3	5	7005/2995	+0.369	11.139
2.00	10.970	6	4	8	6008/3992	+0.178	11.148
2.50	11.145	5	5	10	501/499	+0.002	11.147
3.00	11.335	4	6	20	402/598	−0.173	11.162
3.50	11.505	3	7	30	303/697	−0.362	11.143
4.00	11.740	2	8	40	204/796	−0.591	11.149
4.50	12.070	1	9	80	108/892	−0.917	11.153

$pK_a=11.15\pm0.02$ (using all nine values of the set)

the contents of the titration vessel were thermostated at 25±0.1°C. Pre-saturated nitrogen (with 50 volume per cent aqueous dioxane) was continuously bubbled through the solution. After about 15 min, the titration was started by adding 0.5 m*l* increments of 0.1M KOH each time and noting the highest pH-meter reading which remained steady. Titrations carried out in duplicate were reproducible within±0.01 pH unit. The results of the titration are recorded in Table 1.

Determination of Formation Constants. A weighed quantity of P(n)BHA, corresponding to 0.01M in the final solution of 50 m*l* was transferred to the titration cell and 25 m*l* of dioxane was added to it. Next, 10 m*l* of about 0.005M solution of the metal perchlorate, 5 m*l* of 1M $KClO_4$ and 10 m*l* of water were added to yield a 1: 1 dioxane-water mixture. The titration procedure followed was exactly the same as that described above except that KOH was added in small aliquots of 0.25 m*l* until the pH of the titre solution crossed the hydrolysis point. The results of the copper(II)-ligand titration are summarized in Table 2. For the sake of brevity, results of titrations of Ni(II), Zn(II), and Mn(II) are not given here. The first and second stepwise stability constants, K_1 and K_2, were evaluated by the method of least squares as illustrated by Albert and Serjeant.[12)]

TABLE 2. DETERMINATION OF THE FORMATION CONSTANTS OF Cu(II) COMPLEX WITH *N*-PHENYL-BUTYROHYDROXAMIC ACID

Salt background=0.1M $KClO_4$
Medium=1:1 Dioxane-water
Temperature=25±0.1°C

KOH (0.1M) m*l*	pH	log $[L^-]$	$\bar{n}$	log K_1	log K_2	log K_1K_2
0.00	3.10	—	—	—	—	—
0.50	3.26	$\overline{10}.060$	0.20	a)	a)	a)
1.00	3.47	$\overline{10}.215$	0.41	a)	a)	a)
1.25	3.59	$\overline{10}.304$	0.53	9.66	8.54	18.20
1.50	3.71	$\overline{10}.392$	0.60	9.67	8.56	18.23
1.75	3.84	$\overline{10}.488$	0.72	9.79	8.64	18.43
2.00	4.00	$\overline{10}.611$	0.80	9.77	8.55	18.32
3.00	4.70	$\bar{9}.127$	1.20	9.60	8.63	18.23
3.25	4.90	$\bar{9}.267$	1.31	9.62	8.60	18.22
3.50	5.11	$\bar{9}.408$	1.44	9.59	8.67	18.26
3.75	5.36	$\bar{9}.577$	1.52	9.68	8.51	18.19
4.00	5.66	$\bar{9}.778$	1.64	9.69	8.48	18.17
4.25	6.02[c)]	$\bar{8}.011$	1.70	b)	b)	b)
			Average	9.68	8.58	18.26

a) Discarded.
b) Not calculated as pH crossed the hydrolysis point.
c) No precipitation took place up to this stage of titration.
Result: log $K_1=9.68\pm0.07$, log $K_2=8.58\pm0.06$
log $K_1K_2=18.26\pm0.08$

Results and Discussion

Log K_1, log K_2, and log (K_1/K_2) of the complexes of Cu(II), Ni(II), Zn(II), and Mn(II) are given below. All the constants reported here including pK_a may be termed concentration (or stoichiometric) constants because they were obtained without applying activity corrections. It is quite evident from Table 3 that all the metal chelates are fairly stable. P(n)BHA is believed to react with these metal ions as leading to the formation of a five membered ring in the chelate. On the basis of published data, it has been assumed that P(n)BHA yields 1: 2 complex with the aforesaid metal ions. In the present experiments $\bar{n}$ (average number

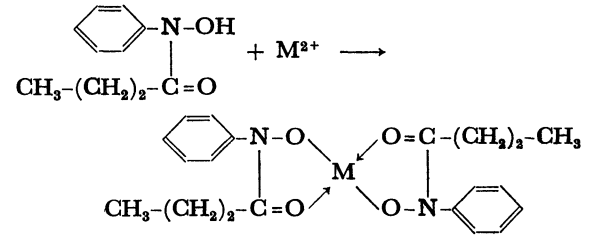


TABLE 3. FORMATION CONSTANTS OF METAL CHELATES

Metal ion	log K_1	log K_2	log (K_1/K_2)
Cu	9.68	8.58	1.10
Zn	6.85	5.52	1.33
Ni	6.67	5.21	1.46
Mn	5.25	4.09	1.16

[12)] Ref. 11, p. 165.

of ligand molecules attached per metal ion) gradually reached a value of nearly 2 before precipitation. So our assumption of 1 : 2 complex formation in solution seems to be valid.

Order of Stability Constants or log K Values. From Table 3 it can be seen that the order Mn<Ni<Cu>Zn is in agreement with that of Irving and Williams.[13] In all the cases $K_1 > K_2$. The values of $\log(K_1/K_2)$ is the highest for the nickel complex. Furthermore, it is observed that the values of log K_2 are lower than log K_1 by approximately 1.1—1.5 units. This suggests that in these systems not only the statistical effect (which gives the value of $\log K_1 - \log K_2 = 0.60$ units) should be considered but the electrostatic effect also becomes important.[14]

Values of log K for copper differs considerably from those for other metals and values for Zn are greater than Ni. The enormously higher log K value for copper chelate may be due to its possible square planar structure. The order Zn>Ni has been observed earlier,[15] where the relatively low value of Ni is attributed to steric hindrance preventing the formation of a square planar structure. Again the hydrolysis constant for Zn is greater than that of Ni indicating a greater affinity of Zn(II) for OH ions. These factors seem to account for the order Zn>Ni.

Financial assistance from the Chemical Society, London and Van't Hoff Fund, Amsterdam is gratefully acknowledged. One of the authors (J.P.S) is indebted to CSIR, New Delhi, for the award of Junior Research Fellowship.

---

13) H. Irving and R. J. P. Williams, *J. Chem. Soc.*, **1953**, 3192.

14) N. Bjerrum, *Z. Phys. Chem.*, **106**, 238 (1932).

15) W. D. Johnston and H. Freiser, *Anal. Chim. Acta*, **11**, 201, 301 (1954).