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SYNTHESIS OF 2-VINYL-8-QUINOLINOL AND MEASUREMENT OF STABILITY OF ITS METAL COMPLEXES

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2-Vinyl-8-quinolinol was prepared in 30% yield from 2-formyl-8-quinolinol by Wittig reaction. The acid dissociation constants of 2-vinyl-8-quinolinol and the stability constants of the chelates of the reagent with some divalent metals have been determined by titration techniques. The chelates are less stable than those of 8-quinolinol and 2-methyl-8-quinolinol.

8-Quinolinol("oxine") has been widely used as organic precipitant[1)] or antibacterial agent.[2)] The introduction of vinyl group into the quinoline ring shows interesting application in the field of polyligands source. Manecke et al.[3)] synthesized 5-vinyl oxine. Its polymer has been found to be effective precipitation reagent for trace metal.[4)] On the other hand, 3-vinyl oxine[5)] and 2-methyl-3-vinyl oxines[6)] which have the vinyl group on the pyridine ring have not been reported in detail. Here we wish to describe the synthesis of 2-vinyl oxine and the chelating tendencies with copper(II), nickel(II), and cobalt(II) ions.

The preparation was carried out according to the similar procedure described in the literature[7)] to a solution of BuLi(4.0 cm^3;2.3 mol/dm^3;9.2 mmol) in dry benzene(80 cm^3) was added triphenylmethylphosphonium bromide[8)](2.86 g;8.0 mmol) over 10 min. After stirring for 4 h under a nitrogen atmosphere a solution of 2-formyl oxine[9)](692 mg;4.0 mmol) in dry benzene(40 cm^3) was added dropwise. The mixture was refluxed for 19 h. Then 10 cm^3 of water and a small amount of 0.1 mol/dm^3 HCl were added in the mixture to afford a weak acidity. The crude product was purified by preparative TLC(hexane:AcOEt=8:2 v/v) and was recrystallized from ethanol-water(6:1 v/v) to give 204 mg(30%) of the desired product as colorless needle; mp 106-109 °C. ^{1}H NMR(s. Fig. 1). IR(KBr): 3100, 1628, 1596, 1560, 1275, and 1090 cm^{-1}. UV(methanol) max: 262(log ε 4.66), 285(3.76), and 316(3.59) nm. Found: C,77.02; H,5.21; N,8.19%. Calcd for $C_{11}H_9NO$: C,77.17; H,5.30; N,8.18%.

The acid dissociation constants(p$\underline{K}$) of 2-vinyl oxine were determined with pH titration in 50 v/v% aqueous dioxane. The titration apparatus consisted of Pyrex vessel maintained in a constant temperature bath, through which could be inserted the tip of a microburet, a thermometer, a nitrogen inlet tube and the extension electrode of a pH meter. The temperature of the solution was kept at 25±0.3 °C. Rapid mixing was achieved by means of a magnetic stirrer. The measurement of pH was carried out with Toa Electronics HM-5BS equiped with GST-155C glass electrode.

The pH meter correction and ion product of water for solution of 50% dioxane were determined to be -0.12 and 15.48, respectively. These results are in agreement with the finding of Irving[10] and Takamoto.[11] The values of $p\underline{K}$ were calculated by the following formulas.[12]

$$p\underline{K}_{NH}=pH-\log\left(\frac{\underline{C}}{\underline{A}-(H^{+})}-1\right)$$

and

$$p\underline{K}_{OH}=pH+\log\left(\frac{\underline{C}}{\underline{B}-(OH^{-})}-1\right)$$

where

$\underline{C}$=concn. of 2-vinyl oxine

$\underline{A}$=concn. of standard acid added to the soln.

$\underline{B}$=concn. of standard base added to the soln.

The $p\underline{K}$ values determined are summarized in Table 1 with results of oxine and 2-methyl oxine. As expected from the resonances effect, $p\underline{K}_{NH}$ is decreased by vinyl substitution in the 2 position in oxine compared with other oxines.[13]

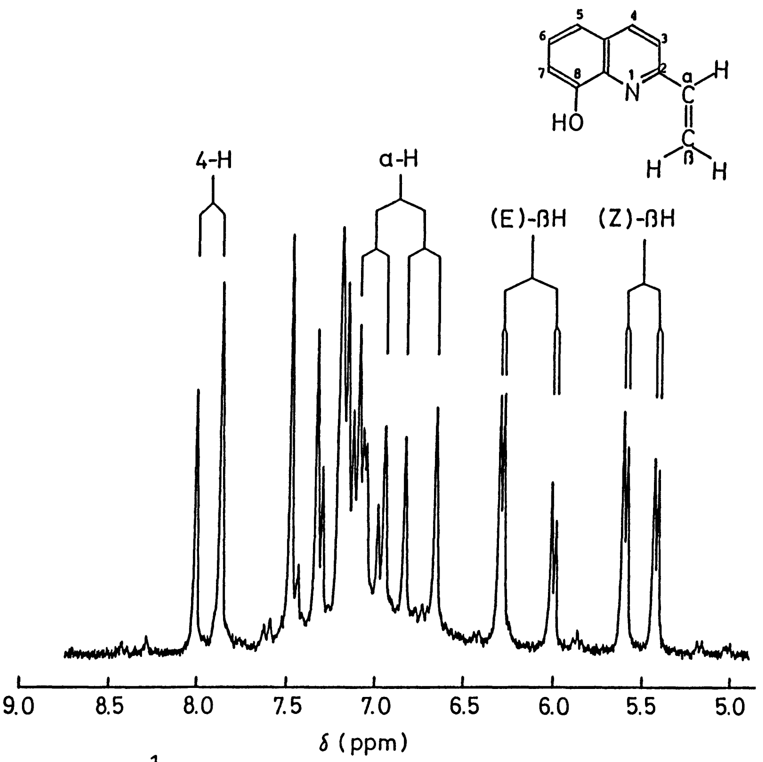

Fig. 1. ^{1}H NMR spectrum of 2-vinyl oxine in $CDCl_3$.

Table 1. Acid Dissociation Constants in 50% Dioxane at 25 °C, μ=0.1(KNO_3)

	$p\underline{K}_{NH}$	$p\underline{K}_{OH}$
2-Vinyl oxine	3.48	11.51
Oxine	4.06 (4.16)	11.30 (11.20)
2-Methyl oxine	4.70 (4.68)	11.78 (11.30)

Values in parentheses are those reported by Stevenson and Freiser.[14]

The stability constants for the formation of the complexes of 2-vinyl oxine with Cu(II), Ni(II), and Co(II) were determined by the Calvin-Bjerrum pH titration technique.[15] The results of representative titration is given in Table 2. Copper was observed to form approximately 1:2 complex with 2-vinyl oxine at pH 6.47. The precipitation[16] was observed above pH 7.48 during titration. The stability constants, $\underline{K}_1$ and $\underline{K}_2$, where $\underline{K}_n=(ML_n)/(ML_{n-1})(L)$, were calculated by means of the method of least squares. The values of log $\underline{K}_1$ and log β_2 are given in Table 3 together with results on complexes of oxine and 2-methyl oxine.

Table 2. Titration of Solution of Metal Perchlorates and Chelating Agent in 50% Dioxane with Sodium Hydroxide at 25 °C, μ=0.1(KNO_3)

0.002 $moldm^{-3}$ 2-vinyl oxine, 0.001 $moldm^{-3}$ $Cu(ClO_4)_2$, 0.0035 $moldm^{-3}$ $HClO_4$, original volume 20 cm^3, concentration NaOH 0.025 $moldm^{-3}$

NaOH(cm^3)	pH value	$\bar{n}$$^{a)}$	$p\underline{R}$$^{b)}$
1.232	3.06	0.240	11.790
1.757	3.23	0.376	11.550
2.174	3.39	0.498	11.337
2.525	3.52	0.644	11.191
2.874	3.67	0.806	11.038
3.165	3.82	0.958	10.900
3.395	3.97	1.091	10.771
3.624	4.15	1.246	10.639
3.884	4.46	1.449	10.429
4.113	5.00	1.663	10.077
4.353	6.47	1.942	9.360

a) $\bar{n}$ is the average number of chelate molecules per metal ion.

b) $p\underline{R}$ is the negative logarithm of the reagent anion concentration.

Table 3. Stability Constants in 50% Dioxane at 25 °C

	2-Vinyl oxine		Oxine		2-Methyl oxine	
	log $\underline{K}_1$	log β_2	log $\underline{K}_1$	log β_2	log $\underline{K}_1$	log β_2
Cu(II)	11.21	21.72	13.88 (13.29)	26.19 (25.90)	12.23 (11.92)	23.61 (22.82)
Ni(II)	7.67	16.22	10.63 (10.50)	19.68 (20.27)	8.88 (8.96)	17.49 (16.94)
Co(II)	7.38	16.63	9.68 (9.65)	18.53 (18.05)	8.95 (8.59)	17.95 (17.38)

Values in parentheses are those reported by Stevenson and Freiser obtained by pH titration at 25 °C.14)

The complexes of 2-vinyl oxine are consistently somewhat less stable than the values for other oxines. The stability data for the complexes of 2-vinyl oxine, however, are close to the tendency observed for 2-methyl oxine.17) The stability constants for Ni(II) and Co(II) chelates of 2-substituted oxine14) may or may not follow the order of stability of the divalent metal ions that has been pointed out by Irving and Williams.18) This strongly suggests that the probable structure of the complex in solution is similar to that of 2-methyl oxine. Thus, some type of steric hindrance due to the 2-vinyl group is operative in the Ni(II) or Co(II) chelates of 2-vinyl oxine.

The acid dissociation constants of 2-vinyl oxine were also determined spectrophotometrically in 50% dioxane at 25±1 °C.19) UV spectra were recorded on a Shimadzu UV 300 spectrophotometer and the absorbance reading at 390 nm were obtained with a SAPCOM 1A spectral data acuisition having processing computer. The absorbance of 2-vinyl oxine increased from 0 to 0.29 with the pH range 6.8 to about 0 and from 0 to 0.67 with the pH from 6.8 to above 14.

The results dealt with in the same manner as titration method. The value of $\mathrm{p}K_{\mathrm{NH}}$ and $\mathrm{p}K_{\mathrm{OH}}$ were 3.41 and 11.62, respectively. The values were in fair agreement with those obtained from titration method.

The stoichiometry of the 2-vinyl oxine and Cu(II) complex was determined by Job's method of continuous variation at pH 6.06. As can be seen from Fig. 2. the chelate compound suggest a 2:1 complex of 2-vinyl oxine to Cu(II).

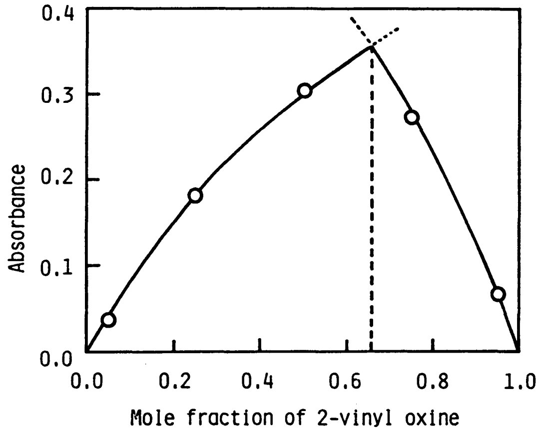

Fig. 2. Continuous variation method on the system of Cu(II) and 2-vinyl oxine in 50% dioxane at 390 nm. Concn. of oxine+Cu; 4×10^{-4} mol/dm^3.

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