Stability Constants of Oximes of 4-Substituted-2-acetylphenols [1]

Y. Shai and A. Warshawsky

Department of Organic Chemistry, Weizmann Institute of Science,
Rehovot 76100, Israel

Abstract. Proton–ligand stability constants (pKd) and metal–ligand stability constants for six oximes of 4-substituted-2-acetyl phenol in H_2O:Dioxane (1:3) are obtained by the spectrophotometric method of Magnusson et al. as modified by Patel et al.

INTRODUCTION

Hydroxyoximes are important phase transfer agents in the hydrometallurgycal recovery of copper [2]. The commerical copper-specific reagents known as Lix-65N (4-nonyl-benzophenone oxime) or Lix-64N [a mixture of 99% Lix-65, and Lix-63 (5,8-diethyl-6-hydroxy-7-oximino dodecane)] belong to this class.

In recent publications, we described a new synthetic route to liquid [3] or polymeric [4,5] hydroxy oximes of types I and II.

I   II
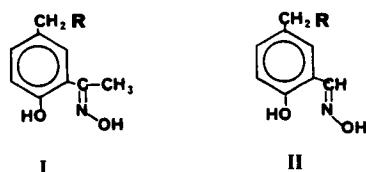
1: R=C_6H_5
5: R=4=methylbenzene
3: R=2,4-dimethylbenzene
4: 4=OCH_2CH_2–O–CH_2–OC_4H_9
5: R=OC_8H_{17}
6: R=$N(C_8H_{17})_2$
7: R=polystyrene
8: R=NH–CH_2-polystyrene

The determination of the stability constants of the oximes of 4-substituted-2-acetyl phenol, in homogeneous media, will provide better understanding of the behaviour of those ligands in phase transfer reactions, or in metal chelation by polymer-bound reagents (6).

EXPERIMENTAL

Oximes 1-6 were prepared as described in Refs. 1 and 6. They were recrystallized and their elemental analysis was in very good agreement with calculated values.

Comp 1 Oxime of 3-acetyl-4-hydroxy-diphenyl methane. mp 100–101°C,

calc:	5.80 %N	6.27 %H	74.66 %C
found:	5.79 %N	6.29 %H	74.62 %C

Comp 2 Oxime of 3-acetyl-4-hydroxy-4'-methyldiphenyl methane. mp 125°C,

calc:	5.42 %N	6.71 %H	75.27 %C
found:	5.31 %N	6.70 %H	75.37 %C

Comp 3 Oxime of 3-acetyl-2',4'-dimethyl-4-hydroxy diphenyl methane. mp 119°C,

calc:	5.20 %N	7.11 %H	75.81 %C
found:	5.24 %N	7.13 %H	75.78 %C

Comp 4 Oxime of n-butyl(3-acetyl-4-hydroxyphenyl) methyl carbitol.

calc:	5.80 %N	6.27 %H	74.66 %C
found:	5.79 %N	6.29 %H	74.62 %C

Comp 5 Oxime of (3-acetyl-4-hydroxyphenyl) methyl octyl ether. mp 57°C,

calc:	4.77 %N	9.27 %H	69.59 %C
found:	4.76 %N	9.29 %H	69.47 %C

Comp 6 Oxime of (3-acetyl-4-hydroxyphenyl) methyl-di(N-octylamine) mp 54°C,

calc:	6.92 %N	10.96 %H	73.86 %C
found:	6.74 %N	10.93 %H	73.89 %C

Proton-Ligand Stability Constants

The determinations are based on the spectroscopic method of Magnusson, Postmus and Craig [7], as modified by Patel, Shah and Patel [8].

510^{-4} M solutions of oximes 1–6 in H_2O:Dioxane (1:3), containing 0.1 M $NaClO_4$. The reagent solution was stirred magnetically and N_2 was passed through the system. A pH electrode coupled to a PHM-62 digital pH meter (Radiometer, Copenhagen) was placed in the solution. The spectrophotometric measurements were taken in 0.5 cm quartz cells, in a Carry 118 spectrophotometer at 348 nm. The spectrum was taken first at pH 3.5, and this gave the value A_{HA}. The pH was then adjusted to 9.50 by capillary injection of 0.1 M NaOH, and the absorption at 348 nm taken again. The pH was varied again and so on.

Metal–Ligand Stability Constants

510^{-4} M solutions of oximes 1–6 in H_2O:dioxane (1:3), and separately, 0.04 M solutions of the metal perchlorates were prepared.

The absorption at 348 nm for the various reagents was measured at pH 2 (Fe), pH 3.5 (Cu), pH 7.0 (Ni, Zn, Co). This gave the corresponding value of A_{HL}. The metal salts were added, allowed to equilibrate at 25 1°C for 5 min, and the absorption at 348 nm was measured again.

RESULTS

The absorption spectra of the ligand recorded at various pH values consists of two bands separated by about 40 nm. The effect of pH is pronounced at 310, 350 and 370 nm, and these wavelengths are, therefore,

suitable for the calculation of pK. Patel, Shah and Patel [8] have shown that for chelates of 2-hydroxy-4-nitro acetophenone, proton—ligand stability constants can be determined reliably at any of the three values with minimal variations (less than 0.1 pK values).

Based on this, we have selected in the present work to calculate pK values derived from measurements at the medium wavelength, namely 348 nm. Thus, the A_{HL} value was determined at 348 nm at pH 3—4, and the value of A_L at the same wavelength at pH 9.50. The constants were calculated by the equations described below, using SAS computer program.

In the equilibrium system:

$$HL + M^{n+} \longrightarrow M^{(n-1)} L^+ + H^+, \quad Ka = \frac{1}{K_d} \qquad (1)$$
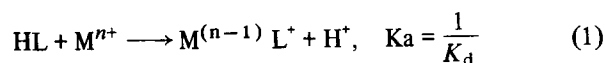
The absorption dependency on hydrogen ion activity is given by the following expression [8]:

$$A = A_{(L^-)} - \frac{a_H (A - A_{HL})}{K_d}$$

where A = absorption at 348 nm at the corresponding pH, A_{HL} = absorption at 348 nm at acidic pH (3—5), A_{L^-} = absorption at 348 nm at highly basic pH, and a_H = hydrogen ion activity.

The plot of A against $a_H(A - A_{HL})$ has a slope of $-1/Kd$, from which Kd is calculated. A typical plot is shown in Fig. 1, for oxime 3.

The pKa values for oximes 1—6 are shown in Table 1. The pKa values are in good agreement with the Lix series, as reported by Ashbrook [9]. Furthermore, the measured pKa values support the anti-oxime structure derived by NMR methods [6].

The behaviour of the oximes with polar substituents in the para position to the phenol, oxime 4 (pKa = 11.78) and 6 (pKa = 12.30), shows deviation from the average value of oximes 1, 2, 3 (average pKa = 12.11) due to hydrogen bonding for the diethyleneglycol comp. 4, or protonation of the amine in comp. 6.

Metal-Ligand Stability Constants

The reaction between a divalent metal cation and a ligand HL is given by Eq. (2):
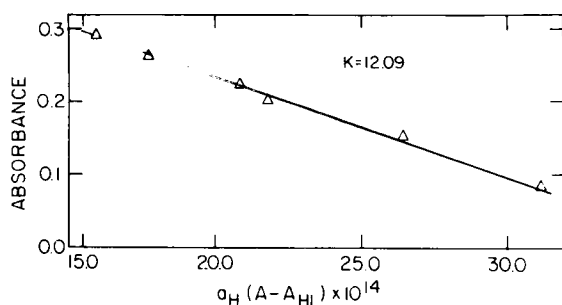

Fig. 1. Plot of absorbance (A) against $a_H(A-A_{HL})$ for oxime 3 at 348 nm, determination of Kd.

Table 1. Proton—Ligand Stability Constants

Oxime	pKd
1 (anti)	12.05
2 (anti)	12.20
3 (anti)	12.09
4 (anti)	11.78
5 (anti)	12.05
6 (anti)	12.30
6 (syn)	10.26
Lix-65N (anti)[a]	12.33[a]
Lix-65N (syn)[a]	10.56[a]
Lix-70 (anti)	11.46[a]
Lix-70 (syn)	9.58[a]

a. Taken from Ref. 9.
Medium: 75% dioxane, 25% water (v/v) T 27° 1°C; C = 0.1 M $NaClO_4$; λ = 348 nm.

$$HL + M^{++} \xrightleftharpoons{K_1} ML^+ + H^+ \qquad (2) \text{ (step 1)}$$

$$HL + ML^+ \xrightleftharpoons{K_2} ML_2 + H^+ \qquad (2) \text{ (step 2)}$$

For salicyl aldoxime and o-hydroxyacetophenone oxime, K_1 is larger than K_2 [10]. Moreover, in phase transfer processes, the first binding step is crucial to the success of the overall transfer. Consequently, it is imperative to establish the value of K_1. To further ensure the predominancy of step 1 in Eq. (2), a five-fold excess of the cation against HL was taken.

The experimental technique used in this work is similar to the method of Patel, Shah and Patel [8] in one variation. Instead of preparing a large number of individual solutions of constant metal and ligand concentrations, at different pH values, which may cause errors and inaccuracies, one reagent solution adjusted to an acidic pH, somewhat lower than the pH value where complexation occurs, was prepared. This was followed by the addition of the metal solution and pH variation by micro-capillary injection of NaOH, without changing the initial volume or concentration of the solution. After each pH adjustment, the absorption at 348 nm was recorded. The absorption at any given pH is provided by the following expression [8]:

$$A = Ax - a_H(A - A_{HL})/K_x.$$

The linear plot of A (at 348 nm) against $a_H(A - A_{HL})$ has a slope of $-1/K_x$, where K_x is given by the expression:

$$K_x = Kd(K_1[M] + 1).$$

K_1 is derived from the above equation, when Kd is known. A typical plot for oxime 3 is shown in Fig. 2 (based on Table 2).

The pK_1 values for the anti-form of the series of the oximes 1—6 and the syn-form of the oxime 6 are given in Table 3.

DISCUSSION

The metal—ligand stability constants K_1, shown in Table 3, can be arranged in the following decreasing order:
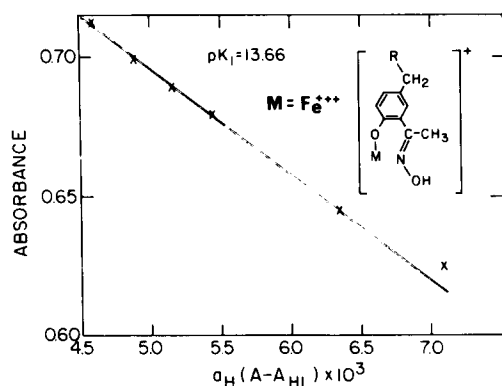
Fig. 2. Plot of absorbance (A) against $a_H(A-A_{HL})$ for oxime 3, determination of K_1.

Table 2. Determination of K_x for Oxime 3 (see Fig. 2)

		$(A_{HL} = 0.011)$		
pH	a_H	A	$A-A_{HL}$	$a_H(A-A_{HL})$
1.94	1.14×10^{-2}	0.625	0.614	7.094×10^{-3}
2.00	1.00×10^{-2}	0.645	0.634	6.340×10^{-3}
2.04	9.12×10^{-2}	0.661	0.650	5.928×10^{-3}
2.09	8.12×10^{-2}	0.679	0.668	5.429×10^{-3}
2.12	7.58×10^{-2}	0.689	0.678	5.143×10^{-3}
2.15	7.08×10^{-2}	0.699	0.688	4.870×10^{-3}
2.19	6.45×10^{-2}	0.713	0.702	4.532×10^{-3}

Table 3. Metal-Ligand Stability Constants (K_1)

	$\log K_1$				
	Fe^{+++}	Fe^{++}	Cu^{++}	Co^{++}	Ni^{++}
1 (anti)	13.36		10.87		
2 (anti)	13.30	12.30	11.11		
3 (anti)	13.66	12.55	11.03	8.55	7.28
4 (anti)	13.00	12.23	11.01	8.30	
5 (anti)	13.32	12.57	10.95		
6 (anti)	13.30	12.29	10.95		
6 (syn)	11.49		8.54	7.58	6.08

1. Medium: 75% dioxane, 25% water (v/v) T 27° 1°C; $C = 0.1$ M NaClO$_4$; $\lambda = 348$ nm.
2. Zn^{2+} was studied. No change in spectrum was recorded.

Fe $>$ Cu $>$ Co $>$ Ni $\gg$ Zn

(Zn^{2+} does not form a complex). This order is in good agreement with the order of metal stability of oximes of 2-hydroxyacetophenone and salicylaldehyde oximes [11]. It is very interesting to note that the variation in the side chain R in Formula (1) shows little effect on the K_1 values. In other words, the metal selectivity of the hydroxyoxime chelating center is hardly influenced by large differences in the side chain at position 4. The variation from aromatic substituents (oximes 1, 2, 3) to glycol (oxime 4), alkylether (oxime 5) or dialkyl-amine (oxime 6) shows a considerable difference in acidity/basicity and hydrophobic/hydrophilic properties of the oximes, without loss of metal specificity. This is of great interest when reagents of large surface activity in phase transfer reactions, or in the development of metal-specific and hydrophilic polymers, are required [5].

The fact that hydroxyoximes 1–6 form stronger complexes with Fe(II) than with Cu(II) points out that the copper selectivity of reagents, such as Lix-65N (2-hydroxy-4-nonyl-benzophenone oxime) [9] in the liquid–liquid extraction of Cu(II) from Cu(II)/Fe(III) sulphuric acid solutions, is not a true thermodynamic selectivity, but probably lies in kinetic preference of Cu(II) binding on the interphase or better solubility of the square-planar CuL_2 complex over the octahedral FeL_3 complex, in the organic phase.

REFERENCES AND NOTES

1. Taken from the M.Sc. Thesis of Yehiel Shai, Feinberg Graduate School, Weizmann Institute of Science, 1979.
2. D.S. Flett, Trans. Inst. Min. Metall., 83, C30 (1974).
3. A. Warshawsky, Int. Solv. Ext. Conf. ISEC-77 Toronto, September 1977, Paper No. 3.
4. A. Warshawsky, R. Kalir and A. Patchornik, J. Org. Chem., 43, 3151 (1978).
5. A. Warshawsky, A. Deshe, B. Rossey and A. Patchornik, Reactive Polymers, 2, 310 (1984).
6. A. Warshawsky, A. Deshe and Y. Shai, in preparation.
7. L.B. Magnusson, C. Postmus and C.A. Craig, J. Am. Chem. Soc., 85, 1711 (1963).
8. C.B. Patel, J.R. Shah and R.P. Patel, J. Inorg. Nucl. Chem., 37, 852 (1975).
9. A.W. Ashbrook, Hydrometallurgy, 1, 6 (1975).
10. K.E. Jabalpurwala, K.A. Venkatachalam and M.B. Kabadi, J. Inorg. Nucl. Chem., 26, 1011, 1027 (1964).
11. A. Warshawsky, Angew. Makromol. Chem., 109/110, 171 (1982).