



CHAPTER I

GENERAL INTRODUCTION

1.1 Oximes and Their Chemistry

Oximes (oxy-imines) are derived from aldehydes or ketones by replacement of the oxygen atom of the aldehyde group (aldoximes) or the keto group (ketoximes). The oxime group (C=N-O-H) is amphoteric, having a slightly basic nitrogen atom and a mild acidic hydroxyl group. Two main structures (A) and (B) (Fig. 1.1) are proposed for the oxime group by Brandy (1), with evidence for an equilibrium between them.



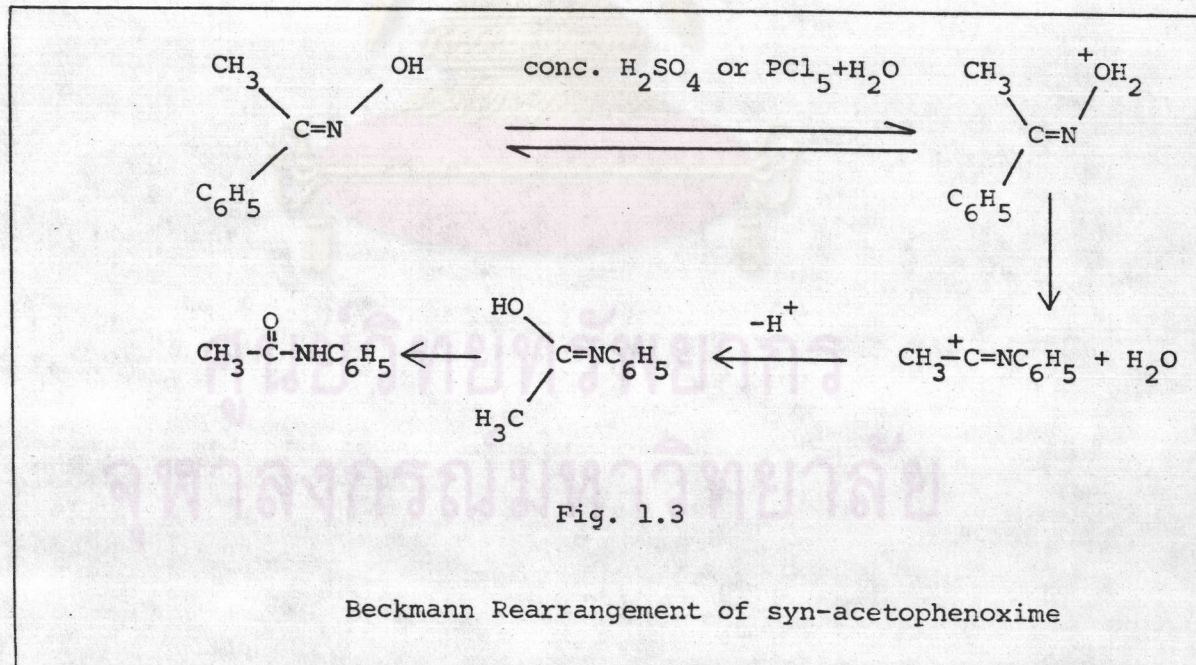
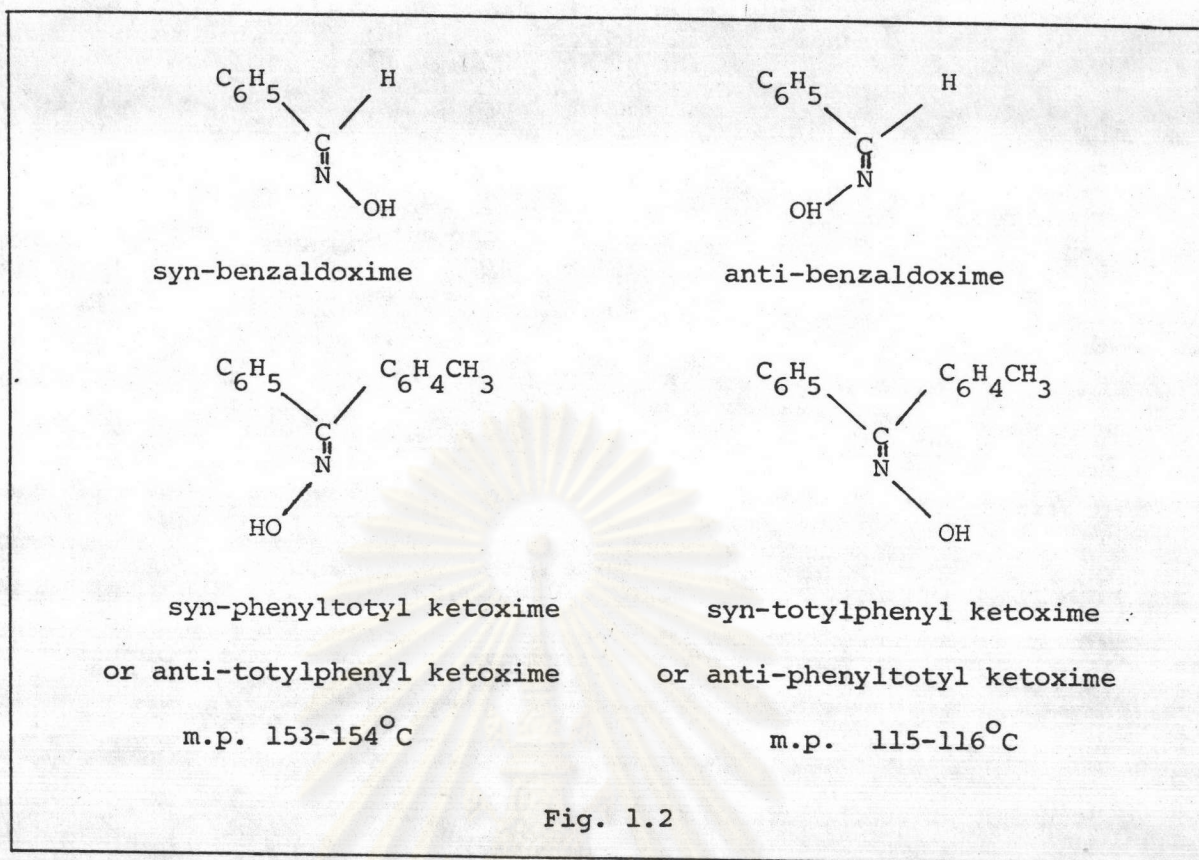
Fig. 1.1

In the neutron diffraction work on dimethylglyoxime, Hamilton (2) established the presence of O-H bonds, favouring structure (A). Usually oximes are associated in the solid state by hydrogen-bonding (O-H.....N). The general method for the preparation of aliphatic and aromatic oximes has been outlined by Vogel (3). Oximes are usually prepared by the addition of hydroxylamine to aldehydes or ketones. They are very stable and can readily be purified by recrystallization and have characteristic, sharp melting points.

Oximes exhibit geometrical isomerism caused by the restricted rotation around carbon-nitrogen double bonds. This was first described

by Hantzsch and Werner (4). Analogous to the cis-trans isomerism in carbon-carbon double bonded compounds, the term syn and anti are used instead of the term cis and trans. For the aldoximes the prefixes refer to the relative positions of the hydrogen and hydroxyl group, and for the ketoximes they refer to the relative positions of the hydroxyl group and the group adjacent to the prefix (Fig. 1.2). The two isomers are different in some properties such as melting point. The configuration of the isomeric forms can be controlled, at least in some cases by determination of the dipole moments of properly substituted aldoximes and ketoximes, choices of a suitable solvent and temperature. Some aldehydes and ketones do not give isomeric oximes, probably because one form is much more stable than the other. The method of determining the configuration of the oxime is an acid-catalyzed transformation of ketoxime to an amide called "Beckmann Rearrangement" (5). When oximes are treated with concentrated H_2SO_4 , PCl_5 and ether, $HCl-HOAc-Ac_2O$, or polyphosphoric acid, the intramolecular migration of the anti R' group to the hydroxyl group of the oxime takes place from carbon to nitrogen atom of the oxime group as shown in Fig. 1.3.

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1.2 Oximes as Metal Chelating Reagents (6,7)

The oxime group has two donor atoms, N and O, and may co-ordinate to a metal atom through either or both, thus acting as unidentate or bidentate, respectively. Oximes can react either as such or in the form of the conjugate base. (Fig. 1.4)

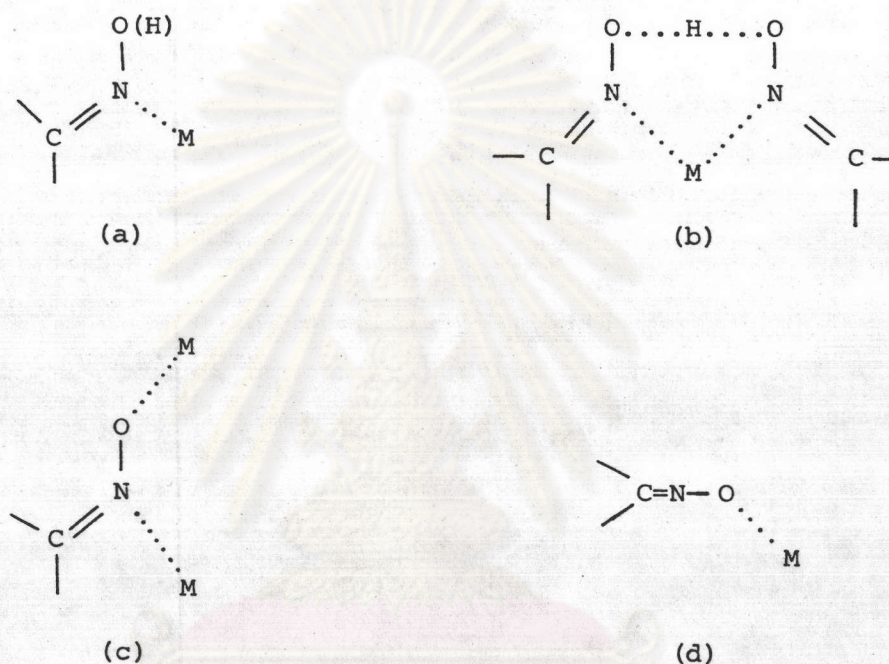


Fig. 1.4

Oximes react with metal ion in the form of the conjugate base. The structural type (a) and (b) are quite common. The type (c) is known in polynuclear species, whereas only a few complexes belong to type (d).

The mode of co-ordination of the oxime group may be greatly influenced by the other group(s) present in ligand. The oxime group may be the sole co-ordinating group present or accompanied by another donor group. Structures of some oxime chelates are known and elucidated by infrared spectrometry, NMR, X-ray and magnetic measurement, etc.

The simplest aliphatic-aromatic ketoxime, acetophenoxime (Fig. 1.5), have long been known and widely studied with respect to its chelating ability and applications in analytical chemistry. Talwar and Haldar (8-10) examined the potentialities of this reagent as metal gravimetric and solvent extraction metallochromic reagent for determination of some bivalent metal ions, Pd(II) and Fe(II) with metal-reagent ratio 1:2, down to the range of 0.1-10, 1-30 and 2-30 microgram respectively.

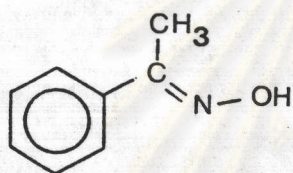


Fig. 1.5

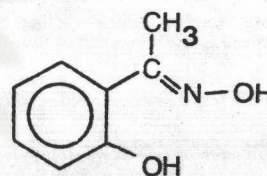


Fig. 1.6

In 1963 Poddar (11) has used o-hydroxy acetophenoxime (Fig.1.6) (HAO : 2-hydroxy acetophenoxime) as a colorimetric reagent for Fe(III) at pH range 2.0-2.5 ($\lambda_{\max} = 570 \text{ nm}$) and 3.7-8.5 ($\lambda_{\max} = 420 \text{ nm}$). It was also used for gravimetric estimation of vanadium by direct weighing of the complete precipitate at pH 2.2 to 4.8 and was found to be quite satisfactory reagent for this purpose because of the great thermal stability and increased insolubility of metal complexes (12). It was recommended that the reagent may be comparatively more selective than acetophenoxime, due to the positioning of the hydroxyl group at the ortho positions with respect to the C=N bond on the phenyl ring of the acetophenoxime. The oxygen atom or the hydroxyl group may act as another donor atom in the reagent molecule including N and O atom of the oxime

group. This hydroxy oxime forms bis-chelated with most bivalent ions, with closed structure due to formation of additional ring by means of interligand and metal interaction in suitable distance and direction. In general, hydroxy oximes form square planar bis-chelates with most bivalent ions (Fig. 1.7)

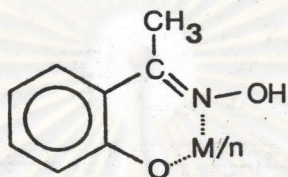


Fig. 1.7

With the expectation that the substitution(s) in the phenyl ring of the o-hydroxy acetophenoxime may make it specific to certain cation, more powerful in complex formation, amplifying sensitivity in determining the amount of that cation, increasing or decreasing solubility of the complexes in aqueous solution, mono substituted and di substituted derivatives of o-hydroxy acetophenoxime also have been prepared. Chawdary and Appalaraju (13) reported the complexes of resacetophenoxime (2,4-dihydroxy acetophenoxime) with Fe (III) spectrophotometrically. Patel and Gaswami (14) used the reagent as indicator for the direct EDTA titration of Fe (III) in the pH range 2.0-3.0 with accuracy $\pm 2\%$.

Saksena and Pandey* (15) made detailed study of reaction of many ions with 5-chloro-2-hydroxy-4-methyl acetophenoxime and it was observed that the reagent can be used as a gravimetric reagent for Cu (II) and

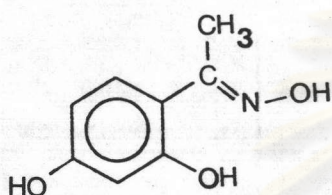
Ni (II). Lal, Gupta and other Indian chemists made further studies of chelate formation of 5-chloro-2-hydroxy-4-methyl acetophenoxime with some bivalent metals and used the reagent for spectrometric determination of Pd (II), Cu (II), Ni (II), Co (II) and V (V), gravimetric determination of Pd (II), Cu (II), Ni (II) and V (V), and complexometric titration of Fe (III) as shown in Table 1.1.

Table 1.1

Ions	M:L	Range of Detn.	pH	Method	Ref.
V(V)	1:2	5.1-30.0 ppm	2.5-4.0	spectro.detn. (400 nm)	16
	1:2	up to 2.54 mg		CHCl ₃ extraction gravi.detn.	17
Pd (II)	1:2	up to 2.88 mg	2.0	gravi.detn.	18
	1:2	10-40 ppm	3.0	spectro.detn. (400 nm) CHCl ₃ extraction	19
Cu (II)	1:2	up to 6 mg	2.5-10.0	gravi.detn.	20
	1:2	up to 0.95 ppm	3.5	spectro.detn. (640 nm) CHCl ₃ extraction	21
Ni (II)	1:2	up to 6 mg	6.0-10.0	gravi.detn.	20
	1:2	up to 0.44 ppm	8.0	spectro.detn. (580 nm) CHCl ₃ extraction	21
Co (II)	1:2	1.73-10.38 ppm	7.5	spectro.detn. (400 nm) CHCl ₃ extraction	22
Fe (III)		up to 56 ug	2.0-2.5	complexometric titratn. accuracy = \pm 0.5 %	23

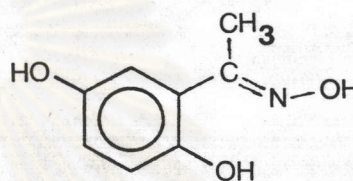
1.3 Reason for Undertaking this Work

It can be seen that o-hydroxy acetophenoxime and its derivatives are comparatively more suitable for analytical work because of their simplicity for synthesis, ease for purification only by recrystallization, high thermal stability, and their potential of specific complexing with some cations.



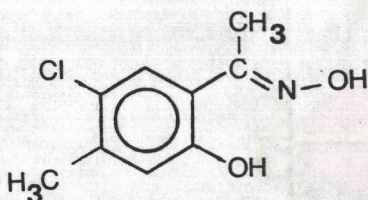
Resacetophenoxime

(2,4-dihydroxy acetophenoxime)



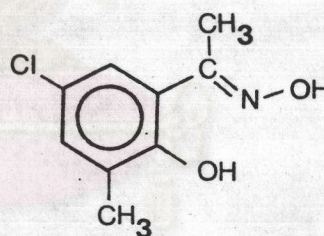
Quinacetophenoxime

(2,5-dihydroxy acetophenoxime)



5-chloro-2-hydroxy-4-methyl

acetophenoxime



5-chloro-2-hydroxy-3-methyl

acetophenoxime

Fig. 1.8

Some mono and di substituted o-hydroxy acetophenoximes

Like their isomers (resacetophenoxime and 5-chloro-2-hydroxy-4-methyl acetophenoxime), it is hoped that quinacetophenoxime and

5-chloro-2-hydroxy-3-methyl acetophenoxime may be used as analytical reagents for both classical and instrumental methods. With some substituted groups on the phenyl ring shift to neighboring position in the two oximes, higher sensitivity and (or) more selectivity can be anticipated.

This work described the attempts to synthesise quinacetophenoxime and 5-chloro-2-hydroxy-3-methyl acetophenoxime, investigate their metal complexing properties, and employ them in analytical work.



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