

A PROPOSED STRUCTURE FOR THE COPPER(II) SALTS OF α -ACYLOIN OXIMES

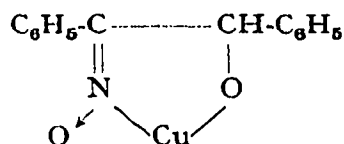
by

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One of the best reagents for the detection and determination of copper (II) is the α -isomer of benzoin oxime, $C_6H_5-CH(OH)-C(NO_2H)-C_6H_5$, introduced into analytical chemistry by FEIGL in 1923⁸. FEIGL, SICHER AND SINGER⁹ established that the ability to form green, water insoluble copper (II) salts is very likely a general property of α -isomers of acyloin oximes. It has been found^{8, 11, 12} that benzoin oxime acts towards copper (II) ions as a "dibasic acid", *i.e.* the hydrogen atoms of both the oxime and the hydroxy groups are replaced by one copper atom. The copper (II) salt of benzoin oxime is characterized by insolubility in most organic solvents and by its inertness towards dilute ammonium hydroxide. Insolubility in ammonium hydroxide, however, is not common to all copper (II) salts of acyloin oximes⁹.

Although it has been well established that for analytical purposes the copper (II) salt of benzoin oxime can be represented by the formula:



the solubility relationships of the compound cannot be satisfactorily reconciled with this structure.

In the present investigation the behavior of copper (II) salts of some acyloin oximes towards various amines was examined in order to study the unusual solubility relationships of these compounds.

The copper (II) salts of the α -acyloin oximes given in Table I were included in the study.

EXPERIMENTAL

A. Organic Preparations

All temperatures are uncorrected and were recorded with a N. B. S. certified thermometer.

The acyloin oximes prepared were obtained as white crystalline solids unless otherwise stated. From the behavior of these acyloin oximes towards copper (II) it is concluded that in all cases only the α -isomer was isolated.

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TABLE I
ACYLOIN OXIMES INVESTIGATED

Name of compound	Formula of compound
Benzoin oxime	$\text{C}_6\text{H}_5-\text{C}-\text{CH}-\text{C}_6\text{H}_5$ $\text{HON} \quad \text{OH}$
2,2'-Furoin oxime	$\text{C}_4\text{H}_3\text{O}-\text{C}-\text{CH}-\text{C}_4\text{H}_3\text{O}$ $\text{HON} \quad \text{OH}$
2,2'-Thenoin oxime	$\text{C}_4\text{H}_3\text{S}-\text{C}-\text{CH}-\text{C}_4\text{H}_3\text{S}$ $\text{HON} \quad \text{OH}$
Phenylbenzoin oxime	$\text{C}_6\text{H}_5-\text{C}-\text{C}(\text{C}_6\text{H}_5)_2$ $\text{HON} \quad \text{OH}$
Methylbenzoin oxime	$\text{C}_6\text{H}_5-\text{C}-\text{C}(\text{CH}_3)\text{C}_6\text{H}_5$ $\text{HON} \quad \text{OH}$
α -Hydroxyisobutyrophenone oxime	$\text{C}_6\text{H}_5-\text{C}-\text{C}(\text{CH}_3)_2$ $\text{HON} \quad \text{OH}$
α -Hydroxyacetophenone oxime	$\text{C}_6\text{H}_5-\text{C}-\text{CH}_2$ $\text{HON} \quad \text{OH}$

Benzoin oxime. The commercially available product, supplied by City Chemical Corporation, was recrystallized from benzene; m.p. 149-150°, m.p. reported³ 150-151°.

2,2'-Furoin oxime. Freshly distilled furfural was condensed with potassium cyanide according to HARTMAN AND DICKEY¹¹. The furoin obtained was oximated with an excess of hydroxylamine hydrochloride in pyridine and methyl alcohol solution. The furoin oxime was finally recrystallized from a mixture of absolute alcohol and petroleum ether "B"; m.p. 157-158°, m.p. reported¹³ 160-161°.

2,2'-Thenoin oxime. This preparation was carried out as described by CARDON AND LANKELMA⁶. The final product had a slight brown discoloration, while the above authors report a white product; m.p. 151-152°, m.p. reported⁶ 142-143°.

Anal. Calcd. for $\text{C}_{10}\text{H}_9\text{NO}_2\text{S}_2$: C, 50.2; H, 3.8; N, 5.9; S, 26.8. Found: C, 50.3; H, 3.9; N, 5.7; S, 26.6.

Phenylbenzoin oxime. Phenylbenzoin was prepared by the addition of phenylmagnesium bromide to benzil according to ACREY¹. The oxime was obtained by the action of hydroxylamine hydrochloride in pyridine and methyl alcohol solution. The product was purified by recrystallization from a mixture of benzene and petroleum ether "B"; m.p. 148-149.5°.

Anal. Calcd. for $\text{C}_{20}\text{H}_{17}\text{NO}_2$: C, 79.2; H, 5.7; N, 4.6. Found: C, 79.4; H, 5.9; N, 4.7.

Methylbenzoin oxime. Methylbenzoin was synthesized following the method described by ROGER¹⁸; methylmagnesium iodide was added to benzil. The oxime was prepared and purified in the same manner as the phenylbenzoin oxime; m.p. 121-122°.

Anal. Calcd. for $\text{C}_{16}\text{H}_{15}\text{NO}_2$: C, 74.7; H, 6.3; N, 5.8. Found: C, 74.8; H, 6.4; N, 5.8.

α -Hydroxyisobutyrophenone oxime: α -Hydroxyisobutyrophenone was prepared by the addition of 0.2 moles of acetone cyanohydrin to one mole of phenylmagnesium bromide in ether solution. After the addition of the cyanohydrin some ether was distilled, replacing it with dry benzene until the temperature of the vapor reached 60°. Stirring under reflux was continued for 6 hours and after standing overnight the mixture was hydrolyzed and the product extracted with benzene. The benzene was flashed off and the residue distilled under reduced pressure. The fraction boiling between 120-130° at 12 mm was collected. Weight: 11.4 g or 35%.

The oxime was prepared by refluxing for 6 hours the ketol obtained with a filtered solution of

hydroxylamine hydrochloride (6.0 g) and potassium hydroxide (5.0 g) in methyl alcohol (100 ml). The product obtained was crystallized twice from a mixture of benzene and petroleum ether "B"; m.p. 114-115°, m.p. reported⁴ 106°.

Anal. Calcd. for $C_{10}H_{13}NO_2$: C, 67.0; H, 7.3; N, 7.8. Found: C, 67.3; H, 7.2; N, 7.7.

α -Hydroxyacetophenone oxime. The oxime was prepared by refluxing for 2 hours a mixture of α -hydroxyacetophenone (5 g) in methyl alcohol (20 ml) with a solution of hydroxylamine hydrochloride (3.0 g) and potassium hydroxide (2.7 g) in water (20 ml). The mixture was extracted with ether and this solution dried over anhydrous sodium sulfate. The residue obtained after evaporation of the ether was crystallized from a mixture of benzene and petroleum ether "B", m.p. 60-70°. Recrystallization from water which contained some ammonium hydroxide gave a product of m.p. 69-70°, m.p. reported¹⁴ 70°.

B. Determination of solubilities

The copper salts of acyloin oximes which are formed in ammoniacal solution were tested for their solubilities in a series of amines. The solubility determinations were performed in the following manner: To ten drops of the acyloin oxime solution contained in a test tube, two drops of an ammoniacal copper(II) solution were added. After the addition of 1 ml of water and thorough shaking, the mixture was centrifuged. The residue obtained was suspended in 1 ml of 95% alcohol and the suspension separated by centrifugation. To the drained residue, 1-2 ml of the amine was added and the mixture homogenized by shaking. After standing for a few minutes, the mixture was centrifuged again.

Solubility terms used in this study: A copper salt was designated as "insoluble" when the supernatant amine was either colorless or so faintly colored as to make a decision difficult. A copper salt was designated as "slightly soluble" (sl. sol.) when the supernatant amine was distinctly colored, but no change in the amount of solid could be observed. A copper salt was designated as "partly soluble" (partly sol.) when a noticeable quantity of the solid dissolved. A copper salt was designated as "soluble" when no noticeable amount of solid remained undissolved.

The following solutions were employed in this study:

- 1) Ammoniacal copper (II) solution: 0.1M copper (II) sulfate (c.p. grade) in 1.0M ammonium hydroxide. pH of this solution was 9.8.
- 2) Acyloin oxime solutions: 0.1M solution of the acyloin oxime in 95% ethyl alcohol.

The amines employed were either c.p. grade or were purified by distillation. Where discoloration of the c.p. grade amine had occurred they were also distilled. The following list gives the sources of the materials as well as the boiling ranges of the purified amines:

Ammonium hydroxide: 27% solution in water. Baker's Analyzed

Methylamine: 25% solution in water. Eastman Kodak.

Ethylamine: 33% solution in water. Eastman Kodak.

isoPropylamine: Eastman Kodak.

Aniline: Eastman Kodak, redistilled. Boiling point of fraction 184-185°.

Ethylenediamine: 95-100%, Eastman Kodak

Diethylamine: The Matheson Co.

Piperidine: Eastman Kodak. The product was dried over solid potassium hydroxide and distilled. Boiling point of fraction: 105-107°.

Methylaniline: Eastman Kodak, redistilled. Boiling point of fraction: 195-196°.

Dimethylaniline: Eastman Kodak.

Triethylamine: Eastman Kodak.

Pyridine: Baker's Analyzed.

α -Picoline: Eastman Kodak, redistilled. Boiling point of fraction: 127-130°.

γ -Picoline: Eastman Kodak, redistilled. Boiling point of fraction: 143-154°.

Quinoline: Eastman Kodak. The product was dried over solid potassium hydroxide and distilled. Boiling point of fraction: 234-235°.

"Versene": 0.2M aqueous solution of disodium salt of ethylenediamine tetraacetic acid. The disodium salt used was supplied by the Alrose Chemical Co. under the trade name of "Sequestrene NA-2".

The colors of the copper salts dissolved in the amines were usually green, varying from a yellow-green to a deep grass-green. Exceptions were the solution colors in ammonium hydroxide, methylamine, ethylenediamine, and versene. In these instances the colors observed were blue, indicating the formation of the respective copper (II) ammine complexes.

The results are collected in Table II.

TABLE II

SOLUBILITY OF COPPER SALTS OF ACYLOIN OXIMES IN DIFFERENT AMINES

Amine	Cu-Benzoin oxime	Cu-Thiobenzoin oxime	Cu-Furois oxime	Cu-Phenylbenzoin oxime	Cu-Methylbenzoin oxime	Cu-3-Hydroxyisobutyrophenone oxime	Cu-3-Hydroxyacetophenone oxime
Ammonium hydroxide	sl. sol.	sl. sol.	soluble	soluble	sl. sol.	partly sol.	partly sol.
Methylamine	sl. sol.	sl. sol.	partly sol.	soluble	insoluble	insoluble	partly sol.
Ethylamine	sl. sol.	insoluble	insoluble	soluble	insoluble	insoluble	partly sol.
isoPropylamine	sl. sol.	insoluble	insoluble	soluble	insoluble	insoluble	partly sol.
Aniline	insoluble	insoluble	insoluble	soluble	insoluble	insoluble	insoluble
Ethylenediamine	soluble	soluble	soluble	soluble	soluble	soluble	soluble
Diethylamine	sl. sol.	insoluble	insoluble	soluble	insoluble	insoluble	insoluble
Piperidine	insoluble	insoluble	insoluble	soluble	sl. sol.	insoluble	sl. sol.
Methylamine	insoluble	insoluble	insoluble	soluble	insoluble	insoluble	insoluble
Dimethylamine	insoluble	insoluble	insoluble	soluble	insoluble	insoluble	insoluble
Triethylamine	insoluble	insoluble	insoluble	soluble	insoluble	insoluble	insoluble
Pyridine	partly sol.	insoluble	partly sol.	soluble	insoluble	sl. sol.	sl. sol.
α -Picoline	partly sol.	insoluble	partly sol.	soluble	insoluble	sl. sol.	sl. sol.
γ -Picoline	partly sol.	insoluble	partly sol.	soluble	insoluble	sl. sol.	sl. sol.
Quinoline	partly sol.	insoluble	partly sol.	soluble	insoluble	sl. sol.	sl. sol.
"Versene"	partly sol.	sl. sol.	partly sol.	partly sol.	sl. sol.	partly sol.	soluble

C. Analysis of copper salts

The copper content of the copper (II) salts of methylbenzoin oxime, thenoin oxime, α -hydroxyisobutyrophenone oxime and α -hydroxyacetophenone oxime was determined by precipitating a known quantity of copper from ammoniacal solution with excess oxime. The compounds obtained were thoroughly washed to remove excess reagent and dried to constant weight at 125-130°. With methylbenzoin oxime and thenoin oxime the excess reagent had to be removed by washing with hot ethanol.

Table III reproduces the results. Although the amounts of copper methylbenzoin oxime and copper thenoin oxime obtained are somewhat high, there is little doubt that the ratio of copper to oxime is in all cases 1:1.

TABLE III

ANALYSIS OF COPPER SALTS OF ACYLOIN OXIMES

Acylain oxime	Weight of copper		Weight of copper salt	
	(grams)	found (grams)	calculated (grams)	found (grams)
2,2'-Thenoin oxime	0.0244	0.1185	0.1155	
	0.0251	0.1215	0.1188	
Methylbenzoin oxime	0.0278	0.1337	0.1325	
	0.0283	0.1378	0.1349	
α -Hydroxyisobutyrophenone oxime	0.0317	0.1209	0.1201	
	0.0325	0.1227	0.1231	
α -Hydroxyacetophenone oxime	0.0244	0.0817	0.0817	
	0.0253	0.0852	0.0847	

DISCUSSION

The present investigation extended the study of the characteristic acylain oxime grouping, $-\text{C}(\text{NOH})-\text{C}(\text{OH})<$, towards copper (II) to four compounds not previously investigated; *i.e.* 2,2'-thenoin oxime, methyl benzoin oxime, α -hydroxyisobutyrophenone oxime, and α -hydroxyacetophenone oxime. These compounds showed the same reactivity as benzoin oxime, the most readily available compound containing the above grouping. All compounds form green, water insoluble copper (II) salts in which the ratio of metal to organic component is 1:1.

The behavior of the copper salts of these acylain oximes as well as the copper salts of benzoin oxime, 2,2'-furoin oxime and phenylbenzoin oxime was tested towards various amines. FEIGL⁸ was the first to note the unusual behavior of the copper (II) salts of acylain oximes towards ammonia. Surprisingly these compounds are insoluble in ammonium hydroxide provided that the acylain is derived from an aromatic aldehyde or an aliphatic aldehyde with more than four carbon atoms. Exceptions to this rule are the copper salts of phenyl- and benzylbenzoin oxime. FEIGL explained the insolubility in ammonia by assuming the copper (II) compounds to be inner complex salts.

DUBSKY AND LANGER⁶ postulate a dimeric formula for copper (II) benzoin oxime as a basic salt. Thermal analysis of the copper salt⁷ showed it to be anhydrous above 60° C. LANGER¹³ proposed a dimeric structure which calls for a coordination number

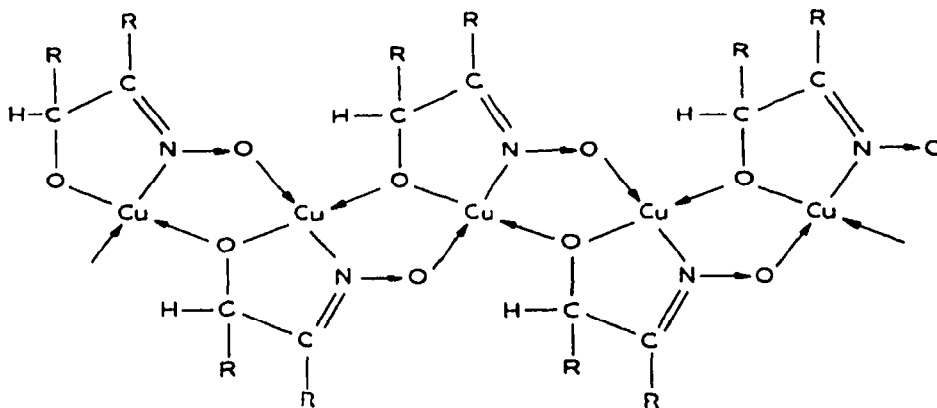
of 3 for the copper. RAY AND SEN¹⁷ conclude from magnetic susceptibility studies that the copper in the copper benzoin oxime compound has a coordination number of 4. They assume for this copper salt an unending chain structure similar to the structure of anhydrous palladium (II) chloride. Steric considerations make their structure rather unlikely.

The insolubility in ammonia of copper salts of acyloin oximes cannot be satisfactorily explained by considering these compounds as inner complex salts. Evidence against this postulate is afforded by the solubility behavior of the copper salts of the oximes of α -hydroxyisobutyrophenone and α -hydroxyacetophenone.

The behavior of the copper salts of acyloin oximes can best be interpreted by assuming a polymeric structure for these compounds. Based on this assumption the insolubility in ammonia can be explained without recourse to coordination to phenyl radicals or multimembered aliphatic radicals. The central copper atom would be shielded from an attack by the ammonia molecule by hydrophobic groups such as phenyl or multimembered aliphatic radicals. The solubility of the copper salts of phenyl- and benzylbenzoin oxime could be explained by the inability of these acyloin oximes to form such polymers because of the size of the organic component. The possibility that the solubility of these compounds in ammonia is to be ascribed to the fact that the hydroxy group in these two acyloin oximes is attached to a tertiary carbon atom can be ruled out from the behavior of the copper salts of methylbenzoin oxime and α -hydroxyisobutyrophenone oxime.

According to PALIT AND McBAIN¹⁸ and PALIT¹⁵ compounds which contain both hydrophobic and hydrophilic groups are soluble in liquids or mixtures of liquids which contain both these groupings. The behavior of the copper salts of acyloin oximes affords some evidence in favor of this postulate. The copper salts studied showed excellent solubility in ethylene diamine, a solvent for the organic component as well as a strong coordinating agent for copper ion. From the blue solution color it can be inferred that decomposition of the copper (II) salts takes place. Pyridine and its homologues which also fulfill the above criteria are fair solvents for copper (II) acyloin oximes.

A structure which seems to fit all available data is given below.



Unfortunately no suitable solvent was found in which molecular weight determinations could be carried out.

SUMMARY

The behavior of the copper (II) salts of the α -isomers of some acyloin oximes towards a series of selected amines was examined in order to study the unusual solubility relationships which these copper salts exhibit towards ammonium hydroxide. The insolubility in ammonium hydroxide of these copper salts of acyloin oximes has been attributed to their being inner complex salts. Evidence is presented which is contrary to this view. Based on the solubilities of the copper (II) salts investigated, a polymeric structure for copper (II) acyloin oximes is proposed.

The study included the following α -isomers of acyloin oximes: benzoin oxime, 2,2'-furoin oxime, phenylbenzoin oxime, methylbenzoin oxime, 2,2'-thenoin oxime, α -hydroxyisobutyrophenone oxime, and α -hydroxyacetophenone oxime. The last four compounds had not been examined previously as to their ability to form copper (II) salts.

RÉSUMÉ

Le comportement des sels de cuivre(II) des α -isomères de quelques acyloinoximes, vis-à-vis d'une série d'amines a été examiné. On a pu ainsi étudier les solubilités anormales que présentent ces sels de cuivre dans les solutions d'hydroxyde d'ammonium. Cette solubilité avait été attribuée au fait que les sels de cuivre forment avec ces oximes des complexes internes, ce qui n'est en réalité pas le cas. En se basant sur les solubilités de ces sels de cuivre(II) une structure polymère est proposée.

Cette étude a été effectuée sur les composés suivants: benzoinoxime, 2,2' furoinoxime, phénylbenzoinoxime, méthylbenzoinoxime, 2,2'-thénoioxime, α -hydroxyisobutyrophénonoxime et α -hydroxyacétophénonoxime. Ces 4 derniers n'avaient pas encore été examinés quant à leur faculté de former des sels de cuivre(II).

ZUSAMMENFASSUNG

Das Verhalten der Kupfer(II) salze der α -Isomeren von einigen Acyloinoximen gegenüber einer Reihe von Ammen wurde untersucht. Auf diese Weise konnte man die abnormalen Löslichkeiten, welche diese Kupfersalze in Ammoniumhydroxyd-Lösungen aufweisen, untersuchen. Diese Löslichkeit ist der Tatsache zugeschrieben worden, dass die Kupfersalze mit diesen Oximen interne Komplexe bilden, was in Wirklichkeit nicht der Fall ist. Gestützt auf die Löslichkeiten dieser Kupfer(II) salze wird eine polymere Struktur vorgeschlagen. Diese Untersuchung wurde mit den folgenden Substanzen ausgeführt: Benzoinoxim, 2,2'-Furoinoxim, Phenylbenzoinoxim, Methylbenzoinoxim, 2,2'-Thenioxim, α -Hydroxyisobutyrophenonoxim und α -Hydroxyacetophenonoxim. Diese vier letzten Substanzen sind bisher noch nicht untersucht worden, in Bezug auf ihre Fähigkeit, Kupfer(II) salze zu bilden.

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