Highly efficient method for oximation of aldehydes in the presence of bis-thiourea complexes of cobalt, nickel, copper and zinc chlorides

Behzad Zeynizadeh* and Serve Sorkhabi*

*Faculty of Chemistry, Urmia University, Urmia 5756151818, Iran

ABSTRACT

In this study, the selective oximation of structurally diverse aromatic aldehydes (versus ketones) to the corresponding aldoxime derivatives was investigated using the combination system of NH$_2$OH·HCl and bis-thiourea complexes of cobalt, nickel, copper and zinc chlorides, M$^{II}$(tu)$_2$Cl$_2$, in a mixture of CH$_3$CN-H$_2$O (1:1). All reactions were carried out successfully at room temperature within the immediate time up to 130 min giving the products in high yields. Investigation of the results exhibited that the applied bis-thiourea metal complexes represented the catalytic activity in order of Co(tu)$_2$Cl$_2$> Ni(tu)$_2$Cl$_2$> Cu(tu)$_2$Cl$_2$> Zn(tu)$_2$Cl$_2$ in their oximation reactions.

Keywords: Aldehydes, Aldoximes, M$^{II}$(tu)$_2$Cl$_2$, NH$_2$OH·HCl, Oximation

1. Introduction

Aldoximes and ketoximes are valuable chemical intermediates that are widely utilized in the chemical industry.$^{1,2}$ They are usually prepared by the reaction of carbonyl compounds and hydroxylamine hydrochloride in the presence of acids or bases including sulfuric acid$^3$, formic acid$^4$, pyridine$^5$, sodium acetate and sodium hydroxide.$^6,7$ Because of some limitations such as low yield of the products, long reaction times and the presence of acid or base sensitive functionalities in aldehyde or ketonic compounds, the classical methods usually are not suitable. In this context, several improvements such as using nano Fe$_3$O$_4$,$^8$ Cu-SiO$_2$,$^9$ NH$_2$OH·HCl/K$_2$CO$_3$,$^{10}$ Dowex 50WX4$^{11}$, heterogeneous polyoxometalates$^{12,13}$, phase transfer catalysts$^{14}$, basic ionic liquid 1-butyl-3-methylimidazolium hydroxide$^{15}$, NH$_3$/oxidant/catalyst systems$^{16-21}$, wet basic Al$_2$O$_3$/microwave$^{22}$, SiO$_2$/NH$_2$OH/microwave$^{23}$, absence of any catalyst and solvent$^{24}$, CaO/solvent-free$^{25}$, TiO$_2$/SO$_4^{2-}$ solid super acid$^{26}$, ethylenediamine/oxone$^{27}$, Na$_2$SO$_4$/ultrasound$^{28}$, titanyl acetylacetonate/NH$_2$OH$^{29}$, Bi$_2$O$_3$/NH$_2$OH·HCl$^{30}$, clay-based titanium silicalite-1$^{31}$, host (dealuminated zeolite Y)-guest (12-molybdo-
phosphoric acid) nanocomposite\textsuperscript{32} and organo-SOMO catalysis\textsuperscript{33} have been reported for the preparation of oximes.

Among the documented catalyst systems for the formation of oximes, most studies are focused on the ammoximation of cyclohexanone and therefore a very limited range of substrates have been investigated. In this context, Sloboda-Rozner reported a sandwich-type polyoxometalate (POM) cluster, Na\textsubscript{12}[W\textsubscript{12}Zn\textsubscript{3}(H\textsubscript{2}O)\textsubscript{2}(ZnW\textsubscript{9}O\textsubscript{34})\textsubscript{2}], which catalyzes the reaction of NH\textsubscript{3} and H\textsubscript{2}O\textsubscript{2} to afford the \textit{in situ} preparation of hydroxyl amine.\textsuperscript{34} As well, the titled POM catalyst activates the nucleophilic surfaces of the resulting hydroxylamine to promote the oximation reaction. The bare Lewis base nucleophilic surfaces are resulted from the external oxygen atoms of W–O–W and W=O species. They act as nucleophilic sites as well as stabilizers of cationic intermediates.\textsuperscript{35-38} In a case for using Na\textsubscript{12}Zn\textsubscript{3}W\textsubscript{19}, however, the oximation reaction was led to low yields of the corresponding aromatic aldoximes due formation of byproducts (amides and nitriles) and carboxylic acids while aliphatic aldehydes were used as substrates. In addition, the inherent acidity of the catalyst can causes the further transformation of the oximation products.\textsuperscript{39-40} Therefore, improving of the selectivity in the oximation of aromatic aldehydes is a subject of more interests. From the industrial aspects, this method suffers from two major drawbacks: relatively high cost of hydroxylamine and the derived serious problems via disposing large amounts of inorganic salts which are co-produced in oximation reactions. Therefore, the requirement for decreasing the use of hydroxylamine in more than stoicho-metric amounts demands the environmental friendly and waste-free procedures as well as the \textit{in situ} preparation of hydroxylamine for the oximation of aldehydes and ketones. Moreover, how to suppress the formation of by-products and increase the selectivity of oximation protocols are of the great significances. Consequently, the short lifetime, insufficient thermal stability and difficulty in recovery of the applied catalyst systems (because of their high solubility in water and polar organic solvents) are the issues which should be taken into account in the development and introduction of new oximation procedures.

In line with the outlined strategies and continuation of our research program directed to the application of bis-thiourea metal complexes of cobalt, nickel, copper and zinc chlorides, M\textsuperscript{II}(tu)\textsubscript{2}Cl\textsubscript{2}, as catalysts for reduction of nitro compounds\textsuperscript{41} and silylation of alcohols\textsuperscript{42}, herein, we wish to introduce a new and highly efficient method for the selective oximation of structurally diverse aromatic and aliphatic aldehydes versus ketones using the combination system of M\textsuperscript{II}(tu)\textsubscript{2}Cl\textsubscript{2}/ NH\textsubscript{2}OH·HCl in a mixture of CH\textsubscript{3}CN-H\textsubscript{2}O (1:1) at room temperature (Scheme 1).

![Scheme 1. Oximation of aldehydes with M\textsuperscript{II}(tu)\textsubscript{2}Cl\textsubscript{2}/NH\textsubscript{2}OH·HCl system](image)

### 2. Results and Discussion

The study was started by the preliminary preparation of bis-thiourea metal complexes of CoCl\textsubscript{2}·6H\textsubscript{2}O, NiCl\textsubscript{2}·6H\textsubscript{2}O, CuCl\textsubscript{2}·2H\textsubscript{2}O and ZnCl\textsubscript{2} as bivalent transition metal leaders of groups 9, 10, 11 and 12 (or VIII, IB and IIB) from Periodic Table (Scheme 2). The complexes were characterized by their physical data and then authorized with the reported data in the literature.\textsuperscript{43}

![Scheme 2. Reaction of bivalent metal chlorides with thiourea](image)
The promoter activity of the prepared complexes on the oximation of aldehyde was then investigated by the reaction of 4-chlorobenzaldehyde as a model compound with hydroxylamine hydrochloride in the absence and presence of MII(tu)2Cl2 complexes at different conditions (Table 1). Observation of the results shows that in the absence of metal complexes, the oximation reactions did not have a reasonable efficiency. Whereas by using any of bis-thiourea metal complexes, the model reaction was carried out perfectly to afford 4-chlorobenzaldoxime as a sole product. Entries 6, 13, 20 and 27 (Table 1) exhibited that using a molar equivalent of MII(tu)2Cl2/NH2OH·HCl (0.2:1.2) per 1 mmol of 4-chlorobenzaldehyde was sufficient to complete the reaction in a perfect efficiency within the immediate time up to 15 sec. In addition, a mixture of CH3CN-H2O (1:1) was the best solvent of choice to progress of the reaction at room temperature. The results also represented that although all of the complexes influenced the oximation of 4-chlorobenz-aldehyde with hydroxylamine hydrochloride, however, the rate enhancement and promoter activity of Co(tu)2Cl2 was greater than the other metal complexes. It is also notable that the oximation of 4-chlorobenzaldehyde with NH2OH·HCl, in the presence of CoCl2·6H2O, NiCl2·6H2O, CuCl2·2H2O and ZnCl2 did not have any impressive results.

Table 1. Optimization experiments for oximation of 4-chlorobenzaldehyde to benzaldoxime with NH2OH·HCl/bis-thiourea metal chloride complexes

| Entry | NH2OH·HCl (mmol) | MII(tu)2Cl2 (mmol) | Conditiona | Time (min) | Conversion (%) |
|-------|------------------|--------------------|------------|------------|---------------|
| 1     | 1.2              | Co(tu)2Cl2 0.5     | THF/reflux | 30         | 95            |
| 2     | 1.2              | Co(tu)2Cl2 0.5     | n-Hexan/reflux | 45         | 20            |
| 3     | 1.2              | Co(tu)2Cl2 0.5     | H2O/reflux | 15         | 95            |
| 4     | 1.2              | Co(tu)2Cl2 0.5     | EtOAc/reflux | 35         | 40            |
| 5     | 1.2              | Co(tu)2Cl2 0.5     | CH3CN/reflux | 45         | 95            |
| 6     | 1.2              | Co(tu)2Cl2 0.2     | CH3CN/H2O (1:1)/r.t. | Immediate | 95            |
| 7     | 1.2              | Co(tu)2Cl2 0.5     | EtOH/reflux | 45         | 30            |
| 8     | 1.2              | Ni(tu)2Cl2 0.5     | THF/reflux | 35         | 90            |
| 9     | 1.2              | Ni(tu)2Cl2 0.5     | n-Hexan/reflux | 45         | 20            |
| 10    | 1.2              | Ni(tu)2Cl2 0.5     | H2O/reflux | 18         | 92            |
| 11    | 1.2              | Ni(tu)2Cl2 0.5     | EtOAc/reflux | 45         | 25            |
| 12    | 1.2              | Ni(tu)2Cl2 0.5     | CH3CN/reflux | 45         | 90            |
| 13    | 1.2              | Ni(tu)2Cl2 0.2     | CH3CN/H2O (1:1)/r.t. | Immediate | 90            |
| 14    | 1.2              | Ni(tu)2Cl2 0.5     | EtOH/reflux | 45         | 25            |
| 15    | 1.2              | Cu(tu)2Cl2 0.5     | THF/reflux | 45         | 85            |
| 16    | 1.2              | Cu(tu)2Cl2 0.5     | n-Hexan/reflux | 45         | 15            |
| 17    | 1.2              | Cu(tu)2Cl2 0.5     | H2O/reflux | 20         | 90            |
| 18    | 1.2              | Cu(tu)2Cl2 0.5     | EtOAc/reflux | 45         | 20            |
| 19    | 1.2              | Cu(tu)2Cl2 0.5     | CH3CN/reflux | 45         | 85            |
| 20    | 1.2              | Cu(tu)2Cl2 0.2     | CH3CN/H2O (1:1)/r.t. | 15 sec | 90            |
| 21    | 1.2              | Cu(tu)2Cl2 0.5     | EtOH/reflux | 50         | 20            |
| 22    | 1.5              | Zn(tu)2Cl2 0.5     | THF/reflux | 50         | 82            |
| 23    | 1.5              | Zn(tu)2Cl2 0.5     | n-Hexan/reflux | 80         | 10            |
| 24    | 1.5              | Zn(tu)2Cl2 0.5     | H2O/reflux | 30         | 80            |
| 25    | 1.5              | Zn(tu)2Cl2 0.5     | EtOAc/reflux | 80         | 20            |
| 26    | 1.5              | Zn(tu)2Cl2 0.5     | CH3CN/reflux | 30         | 75            |
| 27    | 1.4              | Zn(tu)2Cl2 0.4     | CH3CN/H2O (1:1)/r.t. | 15 sec | 80            |
| 28    | 1.5              | Zn(tu)2Cl2 0.5     | EtOH/reflux | 90         | 0             |

*aAll reactions were carried out in 1.5 mL of the solvent.*

The capability of MII(tu)2Cl2/NH2OH·HCl system for oximation of structurally diverse aromatic aldehydes was studied at the optimized reaction conditions. The results of this investigation are illustrated in Table 2. As seen, all reactions were carried out successfully at room temperature within the immediate time up to 65 min to afford aromatic aldoximes in high to excellent yields. The result shows that benzaldehyde can be converted to benzaldoxime in 96% yield (Table 2, entry 1). In the case of electron-releasing substitutions on aromatic rings such as methoxy, methyl and hydroxyl groups, the
corresponding aldoximes can be also obtained in high yields. As well, aromatic aldehydes with electron-withdrawing functionalities including 2-Cl, 4-Cl, 4-F, 3-NO₂ and 4-NO₂ were also successfully converted to the corresponding aldoximes in 82–98% yields using MII(tu)₂Cl₂/NH₂OH·HCl system. Entry 17 represents that this synthetic method is also efficient for the oximation of aliphatic aldehydes via the transformation of citral to citral oxime. It is noteworthy that under the examined reaction conditions, all attempts for the oximation of acetophenone and 4-methoxyacetophenone as ketonic materials with MII(tu)₂Cl₂/NH₂OH·HCl system were unsuccessful.

Investigation of the results (Table 2) exhibited that among the examined bis-thiourea metal complexes, cobalt chloride showed a higher catalytic activity than the other metal chlorides as Co(tu)₂Cl₂ > Ni(tu)₂Cl₂ > Cu(tu)₂Cl₂ > Zn(tu)₂Cl₂. It was proposed that Lewis acid susceptibility of bivalent transition metal cations of first row of Periodic Table and relative stability of the prepared bis-thiourea complexes according to Irving-Williams series⁴⁴,⁴⁵ maybe play a role in their catalytic activities. Co²⁺ with less stable bis-thiourea complex and more Lewis acidity can release thiourea and thus accept NH₂OH as a new ligand for participation in the formation of oximes. In this promotion, however, Zn²⁺ with more d-electrons behaves as less reactive bis-thiourea metal complex for thiourea/NH₂OH ligand displacement.

In order to highlight the promoter activity of MII(tu)₂Cl₂/NH₂OH·HCl system, we therefore compared the oximation of 4-methoxybenzaldehyed with the current protocol and other reported methods. Investigation of the results (Table 3) shows that in view points of the short reaction times, mild reaction conditions, high yields, low loading amounts of NH₂OH·HCl and catalysts, cheapness and easy availability of the catalysts, the present method shows more or comparable efficiency than the other documented protocols.

Table 3. Comparison of the promoter activity of MII(tu)₂Cl₂/NH₂OH·HCl system for oximation of 4-methoxybenzaldehyed with other reported protocols

| Entry | Catalyst (mol% or mg) | NH₂OH·HCl (mmol) | Condition | Time (min) | Yield (%) | Ref. |
|-------|-----------------------|------------------|-----------|------------|-----------|-----|
| 1     | CoII(tu)₂Cl₂ (20 mol%)| 1.2              | CH₃CN-H₂O (1:1)/r.t. | Immediate | 90        | *   |
| 2     | DOWEX 50WX4 (1 g)     | 1.2              | EtOH/r.t. | 40         | 95        | 11  |
| 3     | PMP-POM (400 mg)      | 1.5              | Solvent-free/r.t. | 10         | 100       | 13  |
| 4     | KSF-POM (400 mg)      | 1.5              | Solvent-free/r.t. | 7.5        | 88        | 13  |
| 5     | Al₂O₃-POM (400 mg)    | 1.5              | Solvent-free/r.t. | 10         | 81        | 13  |
| 6     | SiO₂-POM (400 mg)     | 1.5              | Solvent-free/r.t. | 10         | 80        | 13  |
| 7     | TiO₂-POM (400 mg)     | 1.5              | Solvent-free/r.t. | 9          | 86        | 13  |
| 8     | ZrO₂-POM (400 mg)     | 1.5              | Solvent-free/r.t. | 10         | 94        | 13  |
| 9     | K-La(PW11)₂ (25 mol%) | r.t.             |           | 6h         | 86        | 13  |
| 10    | MPA-DAZY (0.6 g)      | 1.2              | Solvent-free/r.t. | 15         | 98        | 13  |

* Present work

3. Conclusions

In this study, bis-thiourea metal complexes of cobalt, nickel, copper and zinc chlorides were prepared and then utilized for the oximation of structurally diverse aromatic and aliphatic aldehydes with hydroxylamine hydrochloride successfully. All reactions were carried out in a mixture of CH₃CN-H₂O (1:1) at room temperature within the immediate time up to 65 min to afford aldoximes in high to excellent yields. The metal complexes showed a prominent catalytic activity as Co(tu)₂Cl₂ > Ni(tu)₂Cl₂ > Cu(tu)₂Cl₂ > Zn(tu)₂Cl₂ in their oximation reactions. Short reaction times, high to excellent yield of the products, easy workup procedure as well as using the commercially available materials are the advantages which make this protocol a synthetically useful addition to the present methodologies.
| Entry | Substrate | Product | \( \text{Co(tu)}_2\text{Cl}_2 \) | \( \text{Ni(tu)}_2\text{Cl}_2 \) | \( \text{Cu(tu)}_2\text{Cl}_2 \) | \( \text{Zn(tu)}_2\text{Cl}_2 \) | m.p. \( ^\circ\text{C} \) Ref |
|-------|-----------|---------|----------------|----------------|----------------|----------------|---------------|
|       |           |         | Molar ratio   | Time (sec) | Yield (%) | Molar ratio   | Time (sec) | Yield (%) | Molar ratio | Time (min) | Yield (%) |               |
| 1     | CHO       | CH=NOH  | 1:1.2:0.2 Im. | 96         |           | 1:1.2:0.2 Im. | 96         |           | 1:1.4:0.4 15 sec | 80         |           | 31\(^\circ\text{C}\) |
| 2     | CHOCl     | CH=NOH  | 1:1.2:0.2 Im. | 95         |           | 1:1.2:0.2 Im. | 90         |           | 1:1.4:0.4 15 sec | 75         |           | 142–146\(^\circ\text{C}\) |
| 3     | CHOF      | CH=NOH  | 1:1.2:0.2 Im. | 98         |           | 1:1.2:0.2 Im. | 90         |           | 1:1.4:0.4 1 min | 90         |           | 85\(^\circ\text{C}\) |
| 4     | MeOCHO    | CH=NOH  | 1:1.2:0.2 Im. | 85         |           | 1:1.2:0.2 10 | 81         |           | 1:1.4:0.4 5 | 78         |           | — |
| 5     | O,NCHO    | CH=NOH  | 1:1.2:0.2 3 min | 82 |           | 1:1.2:0.2 5 min | 82 |           | 1:1.4:0.4 12 | 80 |           | 128–132\(^\circ\text{C}\) |
| 6     | MeOHCHO   | CH=NOH  | 1:1.2:0.2 10 min | 89 |           | 1:1.2:0.2 13 min | 88 |           | 1:1.4:0.4 22 | 80 |           | — |
| 7     | HOCHO     | CH=NOH  | 1:1.2:0.2 Im. | 90         |           | 1:1.2:0.2 15 | 80         |           | 1:1.4:0.4 3 | 85         |           | 69–72\(^\circ\text{C}\) |
| 8     | HOCho     | CH=NOH  | 1:1.2:0.2 13 min | 85 |           | 1:1.2:0.2 17 min | 86 |           | 1:1.4:0.4 35 | 80 |           | — |
| 9     | O,NCHO    | CH=NOH  | 1:1.2:0.2 3 min | 88         |           | 1:1.2:0.2 4 min | 80         |           | 1:1.4:0.4 24 | 78         |           | 121–122\(^\circ\text{C}\) |
| No. | Struct 1 | Struct 2 | Molar Ratio | Sub./NH₂OH·HCl/Cat. | Time | Temp. | Yield (%) | Yield (%) | Yield (%) | Yield (%) |
|-----|----------|----------|-------------|---------------------|------|-------|-----------|-----------|-----------|-----------|
| 10  | ![Struct 1](image1) | ![Struct 2](image2) | 1:1.2:0.2   | 2 min               | 85   | 2 min | 78        | 5 min     | 80        | 180%      |
| 11  | ![Struct 1](image3) | ![Struct 2](image4) | 1:1.2:0.2   | 10 min              | 82   | 1:1.4:0.4 | 2         | 82        | 85–89%    |
| 12  | ![Struct 1](image5) | ![Struct 2](image6) | 1:1.2:0.2   | 21 min              | 85   | 1:1.4:0.4 | 45        | 78        | 58–63%    |
| 13  | ![Struct 1](image7) | ![Struct 2](image8) | 1:1.2:0.2   | 10 min              | 80   | 1:1.4:0.4 | 65        | 80        | 81–84%    |
| 14  | ![Struct 1](image9) | ![Struct 2](image10) | 1:1.2:0.2   | 25 min              | 84   | 1:1.4:0.4 | 13        | 82        | 133–135%  |
| 15  | ![Struct 1](image11) | ![Struct 2](image12) | 1:1.2:0.2   | 30 min              | 83   | 1:1.4:0.4 | 9         | 79        | 72–75%    |
| 16  | ![Struct 1](image13) | ![Struct 2](image14) | 1:1.2:0.2   | 45 min              | 80   | 1:1.4:0.4 | 25        | 82        | —         |
| 17  | ![Struct 1](image15) | ![Struct 2](image16) | 1:1.2:0.2   | 75 min              | 75   | 1:1.4:0.4 | 20        | 78        | —         |

*Molar ratio: Sub./NH₂OH·HCl/Cat. *Im. means immediately. *Yields refer to isolated pure product.
4. Experimental

4.1. General

All reagents and substrates were purchased from commercial sources with high quality and they were used without further purification. FT-IR and \(^1\)H NMR spectra were recorded on Thermo Nicolet Nexus 670 and 300 MHz Bruker spectrometers, respectively. The products were characterized by their \(^1\)H NMR and FT-IR spectra followed by comparison with the authentic ones. All yields refer to isolated pure products. TLC was applied for the purity determination of substrates, products and reaction monitoring over silica gel 60 F\(_{254}\) aluminum sheet.

4.2. Preparation of bis-thiourea metal chloride complexes

To a round-bottom flask (100 mL) containing a magnetic stirrer and the solution of metal chloride (CoCl\(_2\)·6H\(_2\)O, NiCl\(_2\)·6H\(_2\)O, CuCl\(_2\)·2H\(_2\)O, or ZnCl\(_2\)) (0.01 mol, in 20 mL EtOH), an ethanolic solution of thiourea (0.02 mol, 1.52 g in 20 mL) was added. The mixture was stirred under reflux conditions for 4 h. During the progress of the reaction, bis-thiourea metal complex was precipitated. The content of flask was transferred to a Petri-dish for evaporation of the solvent. The residue was washed with absolute ethanol to remove any contaminant. Drying the residue under air atmosphere affords M\(^{1}\)(tu)\(_2\)Cl\(_2\) complex. It is notable that for dissolving thiourea in ethanol, slightly warming was required.

4.3. Typical procedure for oximation of 4-chlorobenzaldehyde with Co(tu)\(_2\)Cl\(_2\)/NH\(_2\)OH-\(\text{HCl}\) system

In a round-bottom flask (10 mL) equipped with a magnetic stirrer, a solution of 4-chlorobenzaldehyde (1 mmol, 0.141 g) in a mixture of CH\(_3\)CN-H\(_2\)O (1:1) (1.5 mL) was prepared. After one min, hydroxylamine hydrochloride (1.2 mmol, 0.083 g) was added and the resulting solution was stirred at room temperature for 30 sec. To the prepared solution, Co(tu)\(_2\)Cl\(_2\) (0.2 mmol, 0.0563 g) was added and stirring of the reaction mixture was continued for 5 sec at room temperature. Progress of the reaction was monitored by TLC (\(n\)-hexane/EtOAc: 5/2). After completion of the reaction, H\(_2\)O (3 mL) was added and the mixture was stirred for 5 min. The aldoxim product was extracted with EtOAc (2 × 4 mL) and the organic layer was then dried over anhydrous Na\(_2\)SO\(_4\). Evaporation of the solvent afforded the pure 4-chlorobenzaldoxime in 95% yield (Table 2, entry 2).

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