CHAPTER 2

REACTIVITY OF OXIMES TOWARDS MIXTURE OF COPPER(II) ACETATE AND BENZOYL PEROXIDE:

Oximes can have versatile reactivities depending on the reaction conditions and reagents used\textsuperscript{2,17,18,56}. Deoximation\textsuperscript{43,107} dehydration\textsuperscript{69,108} and rearrangement\textsuperscript{30,88} are three commonly encountered important reactions of oximes. Efforts have been made to develop newer reagents for these transformations\textsuperscript{109}. Merit of such transformations lies on their versatility, mildness and selectivity. Metal ion mediated/catalysed reactions\textsuperscript{37,44,50,112} can be used as alternative method for these transformations and such reactions have been extensively studied. The results on the use of stoichiometric and catalytic amount of copper(II) compounds in these reactions are limited. Copper(II) sulphate hexahydrate converts tosyl hydrazones derived from ketones or aldehydes to corresponding ketones or aldehydes\textsuperscript{110}. In yet another reaction copper(II) acetate catalyses dehydration of oximes\textsuperscript{73}. However, these reactions require drastic reaction condition.
In the present investigation it is observed that oximes react with a mixture of copper(II) acetate dihydrate and benzoyl peroxide leading to substrate dependent reactions. These reactions mainly lead to dehydration of aldoximes and deoximation of ketoximes. The synthetic and mechanistic study of these reactions are discussed in the following two sections viz. synthetic study and mechanistic study.

2.1 SYNTHETIC STUDY

2.1.1 REACTION OF ALDOXIMES WITH MIXTURES OF COPPER(II) ACETATE AND BENZOYL PEROXIDE

Reactions of aromatic aldoximes with mixtures of copper(II) acetate dihydrate and benzoyl peroxide at room temperature results in dehydration reaction yielding cyanide as the major product (Equation 2.1.1)
Amides as well as aldehydes are also formed in such reactions. This reaction is applicable to several aromatic aldoximes having electron withdrawing as well as electron donating group. Unsubstituted and p-methyl substituted aromatic aldoxime yielded amide as a side product. The yield of various products from such reactions are listed in Table 2.1.1. Copper(II) acetate is known to catalyse such a process without benzoyl peroxide at elevated temperature. Experiments were carried out independently to ascertain the role of each reactant separately. Under the reaction conditions (described in the experimental section) neither copper(II) acetate nor benzoyl peroxide alone can perform these transformations. Copper(II) acetate dehydrates aldoximes under drastic condition, and the present reagent comprising of a mixture of copper(II) salt and benzoyl peroxide achieves this at room temperature. The formation of products like amides and aldehydes are not
Table 2.1.1

Results on reactions of aldoximes with copper(II) acetate and benzoyl peroxide.

<table>
<thead>
<tr>
<th>Entry No</th>
<th>$R^*$</th>
<th>Aldehyde</th>
<th>Nitrile</th>
<th>Amide</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{C}_6\text{H}_5$</td>
<td>10</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>$p-\text{MeC}_6\text{H}_4$</td>
<td>13</td>
<td>42</td>
<td>45</td>
</tr>
<tr>
<td>3</td>
<td>$p-\text{MeOC}_6\text{H}_4$</td>
<td>--</td>
<td>80</td>
<td>--</td>
</tr>
<tr>
<td>4</td>
<td>$p-\text{EtOC}_6\text{H}_4$</td>
<td>--</td>
<td>85</td>
<td>--</td>
</tr>
<tr>
<td>5</td>
<td>$p-\text{ClC}_6\text{H}_4$</td>
<td>--</td>
<td>83</td>
<td>--</td>
</tr>
<tr>
<td>6</td>
<td>$p-\text{Me}_2\text{NC}_6\text{H}_4$</td>
<td>--</td>
<td>80</td>
<td>--</td>
</tr>
<tr>
<td>7</td>
<td>$m-\text{NO}_2\text{C}_6\text{H}_4$</td>
<td>--</td>
<td>90</td>
<td>--</td>
</tr>
</tbody>
</table>

* $R$ has significance as in Equation 2.1.1.
observed in the high temperature reaction of aldioximes with copper(II) acetate alone. Benzyol peroxide can react with oximes in absence of copper(II) acetate at an elevated temperature (refluxing acetonitrile) giving uncharacterised complex product mixture. Benzoic acid is formed as a product in the reaction of oximes with a mixture of copper(II) acetate and benzyol peroxide. Benzyol peroxide is a good radical generating compound and is known for its homolytic and heterolytic cleavage resulting in various radicals. Benzyol, benzyloxy and phenyl radicals are produced in reactions of benzyol peroxide under thermal and photochemical condition. In homolytic cleavage it can give two benzyloxy radical as shown in equation 2.1.2. The benzyloxy radical can give phenyl radical by losing a CO₂ molecule (Equation 2.1.3).

\[
\text{Ph-C-O-O-C-Ph} \rightarrow 2 \text{Ph-C-O}^+ \\
\text{Equation 2.1.2}
\]
Incorporation of these radicals into the oxime should yield functionalised aldoximes. In the systems listed in Table 2.1.1 none of the end products contains a part of the benzoyl peroxide.

The nitriles formed in these reactions are characterised by recording $^1$H NMR and IR spectra after purification. The covalent $C=\!N$ frequency in IR appear around 2200-2250 cm$^{-1}$. The $C=\!N$ frequencies of the compounds are listed in Table 2.1.2. The nitriles that have been prepared (Table 2.1.2) have only aromatic protons along with the protons in the substituent group; thus, the $^1$H NMR are simple. A representative $^1$H NMR spectrum of p-MeO-C$_6$H$_4$-CN is shown in Fig. 2.1.1. The aromatic protons show $A_2B_2$ pattern at $\delta$ 6.96 and 7.6 ppm and the OMe protons appear at 3.87 ppm as singlet. The starting aldoximes has the $-CH(=\!N-)$ proton signal at about 9.5. Disappearance of this signal can be taken as the characteristic evidence for judging
Table 2.1.2

Cyanide frequencies of nitrile compounds prepared.

<table>
<thead>
<tr>
<th>Entry No</th>
<th>Nitrile</th>
<th>Frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C₆H₅CN</td>
<td>2230</td>
</tr>
<tr>
<td>2</td>
<td>p-MeC₆H₄CN</td>
<td>2225</td>
</tr>
<tr>
<td>3</td>
<td>p-MeOC₆H₄CN</td>
<td>2240</td>
</tr>
<tr>
<td>4</td>
<td>p-EtOC₆H₄CN</td>
<td>2215</td>
</tr>
<tr>
<td>5</td>
<td>p-ClC₆H₄CN</td>
<td>2220</td>
</tr>
<tr>
<td>6</td>
<td>p-Me₂N₆H₄CN</td>
<td>2235</td>
</tr>
<tr>
<td>7</td>
<td>m-NO₂C₆H₄CN</td>
<td>2230</td>
</tr>
</tbody>
</table>
Fig. 2.1.1: $^1$H NMR of p-methoxybenzonitrile

p-CH$_3$O-C$_6$H$_4$-CN
complete conversion of aldoximes to the corresponding products.

The amides are characterised by their $^1$H NMR and IR spectra. The $^1$H NMR spectra have the aromatic and substituted alkyl signals along with the amide $-\text{NH}_2$ signal. The identity of $-\text{NH}_2$ proton of amide are ascertained by recording $\text{D}_2\text{O}$ exchange $^1$H NMR (intensity of exchangeable proton signal decreases). Primary amides have their characteristic amide I IR band in the region of 1650 cm$^{-1}$ and amide II band at 1630 cm$^{-1}$. Origin of these two bands$^{114}$ are due to C=O stretching and N-H bending vibrations. The N-H stretching frequencies corresponding to the asymmetric N-H stretching vibrations appear near 3520 and 3400 cm$^{-1}$ respectively. As a representative example, IR of benzamide is shown in Fig. 2.12. Formation of amide can occur through process similar to the Beckmann rearrangement. In this context nickel(II) acetate causes rearrangement of aldoximes. However, analogy of reactivity of nickel(II) acetate and copper(II) acetate does not hold good as the reactions of copper(II) acetate with aldoximes at high temperature (80°C) do
FIG 2:2 IR OF BENZAMIDE IN KBr.
not yield amide but exclusively nitriles are formed. Nickel(II) acetate in contrast gives only the amide. A comparative statement on the reactivities of benzaldoxime with copper(II) acetate, nickel(II) acetate as well as with a mixture of copper(II) acetate and benzoyl peroxide is shown in Table 2.1.3.

In some cases aldehydes are also formed in these reactions (Table 2.1.1). A hydrolytic cleavage of oximes by either copper(II) acetate or a mixture of copper(II) acetate and benzoyl peroxide could be responsible for the formation of aldehydes. Copper(II) sulphate pentahydrate causes deoximation via hydrolytic cleavage; hence controlled experiment was performed by stirring copper(II) acetate and oxime in acetonitrile to see whether deoximation takes place without benzoyl peroxide. This reaction gave negative result suggesting that copper(II) acetate dihydrate in combination with benzoyl peroxide must be responsible for deoximation to yield aldehydes. Aldehydes formed are characterised after purification by column chromatography. The two aldehydes namely benzaldehydes and p-methylbenzaldehyde have their characteristic C=O stretching absorption at 1715 cm⁻¹.
**Table 2.1.3**

Comparative reactivities of benzaldoxime.

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>Reagents</th>
<th>Reaction Condition</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu(OAc)$_2$</td>
<td>80° C, 2 hrs.</td>
<td>Benzonitrile</td>
</tr>
<tr>
<td>2</td>
<td>Ni(OAc)$_2$</td>
<td>80° C, 1 hr.</td>
<td>Benzamide</td>
</tr>
<tr>
<td>3</td>
<td>Cu(OAc)$_2$/BP</td>
<td>R.T., 2 hrs.</td>
<td>Aldehyde, Nitrile &amp; Benzamide</td>
</tr>
</tbody>
</table>
The absorption near 2820 cm$^{-1}$ and 2720 cm$^{-1}$ are corresponding to asymmetric and symmetric C-H stretching vibrations respectively.

These reactions are not applicable to all aromatic aldoximes. Aldoximes like salicylaldoxime failed to give the corresponding nitrile. The reactivity of salicylaldoxime is however different as it gave O-benzoyl derivative as shown in Equation 2.1.4.

\[
\text{NOH} \quad \text{Cu(OAc)$_2$ /BP} \quad \text{CH$_3$CN} \quad \text{XXX}
\]

Equation 2.1.4

The O-benzoylated salicylaldoxime (XXX) is identified from its analytical data and $^1$H NMR and $^{13}$C NMR. The $^1$H NMR spectra of the compound is shown in Fig. 2.1.3A. The signal at 8.7 ppm corresponds to the $\text{-CH(=N-)}$ proton and that at 10 ppm correspond to phenolic $\text{O-H}$ proton. Other aromatic protons appear in the range of 7.3-8.2 ppm as a multiplet. The IR spectrum has a broad
Fig. 2.1.3A: $^1$H NMR of O-benzoylated salicylaldoxime.
weak band near 3300 cm\(^{-1}\) and a sharp but weak band around 1920 cm\(^{-1}\) in addition to its C=O stretching frequency at 1780 cm\(^{-1}\) and C=C frequency at 1600 cm\(^{-1}\) (Fig. 2.1.3B). \(^{13}\)C NMR shows the C=N carbon at 151 ppm and C=O carbon at 162.8 ppm along with the other signals from aromatic carbons in the range of 122-138 ppm (Fig. 2.1.4).

Attempts have been made for choosing different ratios of copper(II) acetate and benzoyl peroxide and oxime to optimise the yield of products. Table 2.1.4 describes such studies with the yield. From yield optimisation experiments thus carried out and from the amount of unreacted oximes the molar ratio of 1:1:5 (copper(II) acetate : benzoyl peroxide : oxime) is found to give the best result.

Reactions of aldoximes with a mixture of copper(II) acetate and benzoyl peroxide are inhibited by protic solvents. For example the reaction does not take place in methanol, ethanol etc. However, the insolvability of copper(II) acetate in dichloromethane, chloroform and toluene have prevented such study in these solvents.
FIG. 2.1.3B. IR of O-Benzoylated Salicylaldoxime in KBr.
Fig. 2.1.4: $^{13}$C NMR of O-benzoylated salicylaldoxime.
**Table 2.1.4**

Amount of recovered oximes in reactions with different ratios of oxime, copper(II) acetate and benzoyl peroxide.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amount of oxime (mmol)</th>
<th>Amount of copper(II) acetate (mmol)</th>
<th>Amount of benzoyl peroxide (mmol)</th>
<th>Amount of recovered oxime (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.35</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0.1</td>
<td>0.5</td>
<td>0.25</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>0.1</td>
<td>0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>4</td>
<td>0.4</td>
<td>0.2</td>
<td>0.2</td>
<td>0.12</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>0.2</td>
<td>0.3</td>
<td>0.2</td>
</tr>
</tbody>
</table>

*Spot intensities are compared on the basis of yield optimisation by the use of TLC.*
2.1.2 REACTION OF KETOXIMES WITH MIXTURES OF COPPER(II) ACETATE AND BENZOYL PEROXIDE

Aromatic ketoximes react with mixtures of copper(II) acetate and benzoyl peroxide to give the parent ketones (Equation 2.1.5). Benzoylation is also no less significant in a few such reactions. Table 2.1.5 shows the products obtained from some ketoximes from the reaction in the presence of mixtures of copper(II) acetate and benzoyl peroxide.

\[
\begin{align*}
\text{Equation 2.1.5} \\
\text{Benzophenone oxime (entry 1) gives benzophenone in 60\% isolated yield. Chalcone oxime (entry 2) is deoximated and the parent ketone is obtained in 70\% yield. Copper(II) cation is known to promote auto-oxidation of } \alpha,\beta\text{-unsaturated ketoximes to give heterocyclic compounds}^2,99. \text{ Here in the case of chalcone oxime it}
\end{align*}
\]
Table 2.1.5: Products of ketoximes (R^1R^2C=NOH) in the presence of copper(II) acetate and benzoyl peroxide

<table>
<thead>
<tr>
<th>Entry No</th>
<th>R^1</th>
<th>R^2</th>
<th>Ketone</th>
<th>Other products</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph</td>
<td>Ph</td>
<td>60%</td>
<td>---</td>
</tr>
<tr>
<td>2</td>
<td>PhCH=CH</td>
<td>Ph</td>
<td>70%</td>
<td>---</td>
</tr>
<tr>
<td>3</td>
<td>Ph</td>
<td>CH₃</td>
<td>40%</td>
<td>(XXXI) 55%</td>
</tr>
<tr>
<td>4</td>
<td>CH₃</td>
<td>CH₃</td>
<td>---</td>
<td>(XXXII) 10%</td>
</tr>
<tr>
<td>5</td>
<td>Ph-CHOH</td>
<td>Ph</td>
<td>60%</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Ph-CO</td>
<td>Ph</td>
<td>45%</td>
<td>(XXXIII) 45%</td>
</tr>
<tr>
<td>7</td>
<td>CH₃-CO</td>
<td>CH₃</td>
<td>10%</td>
<td></td>
</tr>
</tbody>
</table>

![XXXI](image)

![XXXII](image)
has been noticed that deoximation gives chalcone and autooxidation of the initial ketoximes is not taking place.

Exceptional reactivity is observed in the case of acetophenone oxime and acetoxime. In these reactions unspecific complex product mixtures are formed. Acetophenone oxime undergoes deoximation as well as O-benzoylation (entry 3). Deoximation is only 40% and O-benzoyl derivative (XXXI) is obtained to the extent of 55%. The product (XXXI) has been isolated and characterised by IR and $^1$H NMR. The IR spectrum is shown in the Fig. 2.1.5; C=O stretching absorption appears at 1750 cm$^{-1}$ and C=N stretching absorption at 1680 cm$^{-1}$. The $^1$H NMR spectrum (Fig. 2.1.6) shows methyl signal at $\approx$ 2.55 ppm and aromatic proton appears in between 7.3 to 8.25 ppm. Acetoxime probably undergoes C-benzoylation (product XXXII, entry 4) to an extent of 10% only. The major part of the substrate is left unaccounted. This is an indication that acetoxime probably undergoes deoximation to a large extent and the product, acetone, is easily lost during work up of the reaction mixture.
FIG. 21.5 IR OF O-BENZOYLATED ACETOPHENOXIME.
FIG. 2.1.6: 1H NMR of 0-benzoylated acetophenonoxime
In the reactions (entry 1 to 4) copper(II) acetate dihydrate and benzoyl peroxide have been used in only 20 mole % based on the substrate oximes, and thus a catalytic role by these reagents is clear. This reagents have been used in stoichiometric ratio with (+)-benzoin oxime (entry 5) and the ketone formed in 60% yield is not the parent ketone of the oxime but benzil resulting from oxidative deoxygenation of the substrate. A blank reaction of copper(II) acetate dihydrate and benzoyl peroxide in acetonitrile does not yield benzil. Thus possibility of formation of benzil from benzoyl peroxide is ruled out.

2.1.3 REACTION OF BENZILMONOXIME AND DIACETYLMONOXIME WITH COPPER(II) ACETATE AND BENZOYL PEROXIDE:

The oximes derived from 1,2-dione can be either dioxime or monoxime. Both these oximes have
additional co-ordination site than the simple monoximes. Hence, one can anticipate extra stability due to their co-ordination by chelation. It should be possible to isolate stable complexes derived from di-oximes and mono-oximes of 1,2-diones. In fact, there exists a huge literature on the synthesis of 1,2-dioneoxime metal complexes at various oxidation states as well as on the extraction of metal ions at low concentration. In addition to these, the monoximes of 1,2-dione undergo disproportionation reaction leading to the parent dione and the dioxime (Equation 2.1.6).

\[
\begin{array}{c}
\text{R} \text{C} = \text{O} \\
\text{R} \text{C} = \text{NOH}
\end{array}
\xrightarrow{\text{M}^+} 
\begin{array}{c}
\text{R} \text{C} = \text{O} \\
\text{R} \text{C} = \text{NOH}
\end{array}
\]

\text{Equation 2.1.6}

In our study it has been observed that a mixture of copper(II) acetate along with benzoyl peroxide upon reaction with benzilmonoxime leads to the
formation of benzil, 3,4-diphenylfurazan (XXXIII) and benzoic acid (Equation 2.1.7). The benzil is characterised by recording its $^1$H NMR (having only a multiplet around 7.2-7.8 ppm) and also by comparing its IR with that of an authentic sample. There is yet another light yellow compound which has the $^1$H NMR signal at around 7.5-7.2 ppm as multiplet (Fig 2.1.7) and the IR spectrum does not show the C=O as well as the O-H stretching frequencies (Fig. 2.1.8). This compound is characterised to be the 3,4-diphenylfurazan. The mass spectrum (Fig 2.1.9) has its mass at 222 m+/e. The other mass peaks at 192, 118, and 102 support the fragmentation shown below.
Fig. 2.1.7: $^1$H NMR of 3,4-diphenylfurazan
FIG. 21.8 IR OF 3,4-DIPHENYLFURAZAN IN NUJOL.
Fig. 2.1.9: Mass spectrum of 3,4-diphenylfuran
To look into the origin of 3,4-diphenylfurazan, the possibility of an initial disproportionation as in the equation 2.1.6 is exploited. It has been observed that on reaction of a mixture of copper(II) acetate and benzilmonoxime partial deoximation of the intermediate benzildioxime takes place and a mixture of benzil and 3,4-diphenylfurazan is obtained. However, we could not observe the benzilmonoxime from this reaction and has been attributed to the problem in separation of the two oximes namely the benzilmonoxime and benzildioxime in small scale by column and thin layer chromatography. However, on the basis of the results from the Okac et al.\textsuperscript{51} and from the results on the formation of benzil and 3,4-diphenylfurazan, conclusion can be made that the formation of 3,4-diphenylfurazan originates from an initial disproportionation of the benzilmonoxime (Equation 2.1.6). Catalytic reaction of Pd(PPh\textsubscript{3})\textsubscript{2}O\textsubscript{2} with benzildioxime is also known to yield the heterocycle 3,4-diphenylfurazan\textsuperscript{46}. Control experiments performed to check the possibility of reaction of benzilmonoxime and benzildioxime with copper(II) acetate dihydrate alone to give the heterocycle did show negative result.
2.2 MECHANISTIC STUDY

2.2.1 SYNTHESIS OF COPPER 1,2-DIONEOXIME COMPLEXES:

Dimethylglyoxime is a reagent that has found immense use in analytical as well as synthetic inorganic chemistry. This reagent is commonly abbreviated as DMG and used as a reagent for qualitative as well as quantitative detection of nickel. The complexes derived from DMG and cobalt ion at different oxidation states have found use in catalytic Chemistry. The use of DMG in gravimetric estimation is a textbook reaction. The 1,2-dionemonoxyoxime complexes of copper are less studied. Copper(II) complexes of a few 1,2-dioneoxime derivatives of cyclohexane are known. Benzilmonoxime is also used for spectrophotometric estimation of Co, Ir, etc.

The previous section described the experiments designed to study the reaction between oximes and copper(II) acetate under oxidative condition. And these reactions were performed by mixing the reagents together so as to perform one pot reaction. The study of reactivity on isolated oxime
complexes would through light on the mechanistic as well as on the design of the experiment to have better synthetic utility. Thus, the reactivity of isolated Cu$_2$(DMG)$_4$ with benzoyl peroxide was studied. At room temperature we did not observe any significant reaction of this complex with benzoyl peroxide. On having such an observation, we focused our attention on the reaction of diacetylmonoxime with a mixture of copper(II) acetate dihydrate and benzoyl peroxide. A low yield reaction giving 10% deoximated product viz. diacetyl was observed. This result indicated that a ligand exchange process may be required to initiate the process. So to look into more detail of the reaction we have studied only the reaction of diacetyl monoxime with copper(II) acetate. This reaction when carried out in acetonitrile under aerobic condition we observed products which have inconsistent C,H,N analysis. However, on several recrystallisation from acetonitrile and on choosing suitable crystal for crystallographical study it is observed that a dimeric dimethylglyoxime complex is formed. The structure of the Cu$_2$(DMG)$_4$ is shown in Fig. 2.2.1. The structural parameters along with selected bond lengths and bond angles are listed
Fig. 2.2.1: Crystallographic structure of Cu$_2$(DMG)$_4$
in Table 2.2.1. There is no significant difference from the reported structure\textsuperscript{115}.

Formation of dimethylglyoxime complex of copper(II) starting from diacetylmonoxime ligand provided support to the initial disproportionation of the monoxime to the dioxime. The formation of dimethylglyoxime complex could be prevented if the reactions were performed strictly under an inert atmosphere. This observation is supported by the observation of change of optical density at 673 nm (which is the $\lambda_{\text{max}}$ for an acetonitrile solution of copper(II) acetate) on addition of diacetylmonoxime. New $\lambda_{\text{max}}$ at 388 nm were observed, which underwent degradation i.e. the absorbance drastically changed. However, the solution can retain a constant absorbance at $\lambda_{\text{max}}$ 388 nm if the reaction is performed in an inert atmosphere. Thus, the presence of oxygen is a must for observation of such disproportionation as described in equation 2.1.6.

In addition to these for such disproportionation to occur the reaction must accompany the following processes (Equation 2.2.1). Hydroxylamine is an
Table 2.2.1

The structural parameters along with selected bond lengths and bond angles for crystallographic structure of Cu$_2$(DMG)$_4$ (Fig. 2.2.1)

Lattice Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>7.144 (4) Å</td>
</tr>
<tr>
<td>b</td>
<td>17.12 (1) Å</td>
</tr>
<tr>
<td>c</td>
<td>9.798 (4) Å</td>
</tr>
<tr>
<td>β</td>
<td>106.96 (4)°</td>
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<tr>
<td>V</td>
<td>1146 (1) Å$^3$</td>
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Space Group P2$_1$/n (#14)

Z value = 2

$D_{\text{calc}} = 1.883$ g/cm$^3$

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
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<tr>
<td>atom atom distance</td>
<td>atom atom atom angle</td>
</tr>
<tr>
<td>Cu(1) O(3) 2.24</td>
<td>O(3) Cu(1) N(1) 97.2</td>
</tr>
<tr>
<td>Cu(1) N(2) 1.86</td>
<td>O(3) Cu(1) N(3) 91.7</td>
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<td>Cu(1) N(4) 2.03</td>
<td>N(1) Cu(1) N(2) 82.8</td>
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<td>N(4) C(6) 1.26</td>
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<td>Cu(1) O(3) N(3) 103</td>
</tr>
<tr>
<td>Cu(1) N(1) 2.07</td>
<td>Cu(1) N(1) C(1) 109</td>
</tr>
<tr>
<td>Cu(1) N(3) 1.88</td>
<td>Cu(1) N(2) O(2) 129</td>
</tr>
<tr>
<td></td>
<td>Cu(1) N(3) C(5) 117</td>
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<tr>
<td></td>
<td>O(3) Cu(1) N(2) 100.8</td>
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<tr>
<td></td>
<td>O(3) Cu(1) N(4) 103.6</td>
</tr>
<tr>
<td></td>
<td>N(1) Cu(1) N(3) 95.9</td>
</tr>
<tr>
<td></td>
<td>N(2) Cu(1) N(3) 167.5</td>
</tr>
<tr>
<td></td>
<td>N(3) Cu(1) N(4) 82.1</td>
</tr>
<tr>
<td>Cu(1) N(2) C(2) 117</td>
<td></td>
</tr>
<tr>
<td>Cu(1) N(3) O(3) 128</td>
<td></td>
</tr>
<tr>
<td>Cu(1) N(1) O(1) 121</td>
<td></td>
</tr>
<tr>
<td>O(3) N(3) C(5) 113</td>
<td></td>
</tr>
<tr>
<td>Cu(1) N(4) C(6) 111</td>
<td></td>
</tr>
<tr>
<td>N(3) C(5) C(6) 111</td>
<td></td>
</tr>
<tr>
<td>N(4) C(6) C(5) 117</td>
<td></td>
</tr>
</tbody>
</table>
intermediate product which has to be formed in the reaction. Hence, the reactivity of hydroxylamine with the copper ion plays a crucial factor in deciding the fate of the complex. Hydroxylamine is a strong reducing agent that has been extensively studied\textsuperscript{116}. It can react with copper(II) ion to reduce it to copper(I) or to the metallic copper\textsuperscript{117}. It can also form copper complexes of various compositions. Some isolated and characterised complexes of copper(II) are Cu(NH$_2$OH)$_4$Cl$_2$, Cu(NH$_2$OH)$_4$(NO$_3$)$_2$ \textsuperscript{118}. It is described in the literature that hydroxylamine reduces copper(II) to copper(I) and the redox properties of NH$_2$OH are dependent on the acidity of the medium. In addition to these, the reactivity of hydroxylamine is also solvent dependent. However, the hydroxylamine copper(II)
complexes are less stable and some of them are explosive. In such decomposition the following reactions predominates (Equation 2.2.2). We pursued to

\[
\text{Cu}^{2+} + n\text{NH}_2\text{OH} \rightarrow \left[\text{Cu}\left(\text{NH}_2\text{OH}\right)_n\right]^{2+} + n\text{H}_2\text{O} \rightarrow \frac{3n-1}{2}\text{H}_2\text{O} + \frac{n}{2}\text{N}_2 + \text{H}^+ 
\]

**Equation 2.2.2**

synthesize the copper(II) diacetylmonoxime complex and also study its reactivity with benzoyl peroxide and study its degradation under aerobic condition. The addition of diacetylmonoxime to copper(II) acetate under nitrogen atmosphere gave a homogeneous green solution; this solution on evaporation under reduced pressure and repeated wash with dichloromethane/hexane mixture under nitrogen atmosphere gave a green complex. The complex has the composition \([\text{Cu(DAM)(DAMH)(OAc)}]1.5\text{CH}_3\text{CN}\) (where DAM = anion of diacetylmonoxime, DAMH = diacetylmonoxime, OAc = acetate ion). The comparison of the IR spectra of the complex and its free ligands supports the co-ordination
of oximes along with the presence of an acetato group (Fig. 2.2.2A and 2.2.2B). The carbonyl frequency of acetato group appears at 1600 cm\(^{-1}\) suggesting it to be a chelating. The C=N bond frequency, which in the free oxime appears at 1540 cm\(^{-1}\), is shifted to 1560 cm\(^{-1}\). The \(\text{O-H}\) frequency that appears in the free ligand at 3200 cm\(^{-1}\) is shifted towards 3300 cm\(^{-1}\). The carbonyl frequency of the free ligand at 1670 cm\(^{-1}\) is shifted to 1680 cm\(^{-1}\). These suggest that the co-ordination of diacetylmonoxime occurs via two co-ordinating site viz. C=O and C=NOH. There is a weak absorbance at 2220 cm\(^{-1}\) due to the co-ordinating acetonitrile. It has not been possible to obtain crystalline compound to ascertain the three dimensional structure but the presence of an additional neutral diacetylmonoxime ligand may be an indicative of oligomeric compound\(^{18,51}\). The presence of neutral ligand in oxime complexes is not an unusual phenomenon as complexes having neutral oximes are encountered very often, e.g. Ni(L)(LH)(OH) is a reported compound \(^{51}\). The oxime complex thus formed can undergo deoximation reaction on reaction with benzoyl peroxide.
FIG. 2-2-2A IR OF DIACETYLMONOXIME IN KBr.
FIG. 2 - IR OF DIACETYLMONOXIME COMPLEX WITH COPPER(II) ACETATE.
Although it has been possible to isolate and characterise the diacetylmonoxime copper(II) complex, attempt to prepare the analogous copper(II) complex of benzilmonoxime resulted in the formation of a dark red copper(I) complex with the composition [Cu(BMA)]\(_{1.5}\) CH\(_3\)CN. This complex is characterised by recording its NMR, IR and elemental analysis. The IR and NMR spectra are shown in the Fig. 2.2.3A and 2.2.3B. The peaks at 1660 and 1580 cm\(^{-1}\) are due to the C=O and C=N stretching frequencies respectively. The aromatic protons of the compound appear as broad signal around 7.5 ppm, the methyl group of the co-ordinated acetonitrile appears at 2.19 ppm as a singlet. The complex is stable in solid state; however, it degrades in solution.

As already pointed out in equation 2.2.1 that the disproportionation reaction is to be accompanied by the hydroxylamine formation, the formation of copper(I) complex supports such observation. We have also attempted to study the reaction of hydroxylamine hydrochloride as well as hydroxylamine with copper(II) acetate in aqueous and in acetonitrile as solvent. In
FIG 2.2.3A IR OF BENZILMONOXIME COMPLEX WITH COPPER (II) ACETATE IN KBr.
Fig. 2.2.3B: $^1$H NMR of benzilmonoxime complex with copper(II) acetate in CDCl$_3$.
aqueous medium hydroxylamine hydrochloride on reaction with copper(II) acetate precipitates CuCl and gas evolution takes place. The IR of the precipitate (Fig. 2.2.4) suggests it to be CuCl as there is no other peak than nujol. The estimation of copper and chloride ion also support it to be CuCl. The same reaction in acetonitrile resulted in a colourless solution without evolution of gas. The colourless solution thus formed turns dark yellow having $\lambda_{\text{max}}$ at 455 nm suggesting it to be CuCl$_2$. It may be emphasised that the reactivity of hydroxylamine varies with the variation of the metal ions. For example the [IrCl$_6$]$^{2-}$ reacts with hydroxylamine in acidic medium yielding nitrogen gas, whereas the reaction of hydroxylamine with Fe$_2$(SO$_4$)$_3$ in neutral condition results in the formation of N$_2$O gas along with the reduction of ferric salt to ferrous salt.

2.2.2 VISIBLE SPECTROSCOPIC STUDY:

Visible spectroscopic study is performed to ascertain the role of copper(II) oxime complex taking part in these reactions. Oximes can form complexes with copper(II) ion$^{18}$. Copper(II) acetate itself has a
FIG. 2-2C \( \text{IR of Copper(I) Chloride in Nujol} \).
dimeric structure and the interaction of an oxime with such a dimer is expected to be more complicated than interaction of oxime with a monomeric copper(II) salt (such as CuCl₂). Complexes derived from monoxime ligand without additional functional groups are found to be less stable. In this context, 1,2-dione oximes are expected to have more stability when a copper(II) complex is derived from such an oxime. Thus, 1,2-dione oximes may form chelated copper(II) complexes with lesser reactivity than analogous monoxime complex without having an additional binding site and thus would suit kinetic study. An acetonitrile solution of copper(II) acetate dihydrate absorbs at 673 nm. Intensity of this absorption decreases on addition of benzilmonoxime and a new absorption maximum at 418 nm appears. The band is presumably due to a ligand to metal charge transfer transition. The visible spectrum of a solution containing excess of benzilmonoxime is shown in Fig. 2.2.5. However, absorbance at 418 nm spontaneously reaches a maximum on addition of excess benzilmonoxime solution and decays to reach an optimum value after a lapse of time. The change of absorbance
Fig. 2.2.5: Visible spectrum of copper(II) acetate with excess of benzilmonoxime in acetonitrile.
at 418 nm as an exponential form is shown in Fig. 2.2.6. Absorbance of solution of copper(II) acetate and benzilmonoxime in four different concentrations at 418 nm after they reach their optimum value at 25°C are recorded (Table 2.2.2). On plotting absorbance against concentration we have observed a linear relationship (Fig. 2.2.7). This suggests that benzilmonoxime can be estimated quantitatively by using copper(II) acetate. Spectrophotometric estimation of cobalt and iridium by benzilmonoxime is reported. Isobestic point at 595 nm is observed on gradual addition, in separate aliquot, of benzilmonoxime solution (in acetonitrile) to a copper(II) acetate solution (Fig. 2.2.8). By isobestic point we mean a wavelength at which no change of absorbance occurs while one species is interconverting with another species. Hence occurrence of such a point in the process of interconversion suggests one is to one conversion of one species to another (Equation 2.2.3).

\[
\text{CH}_3\text{CN} \\
\text{Cu}_2(\text{OAc})_4 + n\text{BMO} \rightleftharpoons \text{Cu}_2(\text{OAc})_{4-n}\text{(BMA)}_n + n\text{AcOH}
\]

Where BMA = Benzilmonoxime anion, BMO = Benzilmonoxime.

Equation 2.2.3
FIG. 2.2.6 THE CHANGE IN ABSORBANCE AT 418 NM OF AN ACETONITRILE SOLUTION OF A MIXTURE OF COPPER(II) ACETATE DIHYDRATE (9.5 × 10^{-4} MOL DM^{-3}) AND BENZIL MONOXIME (5.3 × 10^{-3} MOL DM^{-3})
Table 2.2.2
Absorbance at 418 nm of a mixture of copper(II) acetate and benzilmonoxime in different mol ratios.

<table>
<thead>
<tr>
<th>Mol ratio of copper(II) acetate to benzilmonoxime</th>
<th>Absorbance at 418 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 5</td>
<td>0.130</td>
</tr>
<tr>
<td>1 : 6</td>
<td>0.158</td>
</tr>
<tr>
<td>1 : 7</td>
<td>0.175</td>
</tr>
<tr>
<td>1 : 8</td>
<td>0.190</td>
</tr>
</tbody>
</table>
Fig. 2.2.7: Linear relationship between absorbance at 410 nm and mol ratio of copper(II) acetate to BMO.
Fig. 2.2.8: Isobestic point at 595 nm on gradual addition of benzilmonoxime to copper(II) acetate solution in acetonitrile.
In a study performed by Munakata et al.\textsuperscript{121} have shown that by knowing the concentration of the various absorbing species at various ligand concentrations one can find out the composition of such a complex. To evaluate $n$ in equation 2.2.3 formulation is being made as follows:

$$K_C = \frac{[\text{Cu}_2(\text{OAc})_4-n\text{ (BMA)}_n][\text{AcOH}]^n}{[\text{Cu}_2(\text{OAc})_4][\text{BMO}]^n}$$

$$\log R = \log K_C - n \log [\text{BMO}]$$

where,

$$R = \frac{[\text{Cu}_2(\text{OAc})_4-n(\text{BMA})_n][\text{AcOH}]^n}{[\text{Cu}_2(\text{OAc})_4]} \propto \frac{A_C - A}{A_0 - A_C}$$

\textbf{Equation 2.2.4}

$A_C$ is the absorbance at a concentration, $c$, of benzilmonoxime in acetonitrile solution of copper(II) acetate, $A_0$ is the absorbance of copper(II) acetate solution at the beginning and $A$ is the final absorbance at 673 nm. Variation of absorbance at 673 nm with the increase of benzilmonoxime concentration is shown in Table 2.2.3. Since there is no measurable $\lambda_{\text{max}}$ to measure the concentration of BMO, we have assumed the
**Table 2.2.3**

Equilibrium study of benzilmonoxime and copper(II) acetate in acetonitrile — variation of absorbance at 673 nm versus benzilmonoxime concentration.

$A_0 = \text{Absorbance of copper(II) acetate alone} = 0.1809$

$A = \text{Final absorbance (}A_c\text{)} = 0.0966$

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>Volume of BMD</th>
<th>Concentration of BMD in mol dm$^{-3}$ (C)</th>
<th>Absorbance</th>
<th>$A_c$</th>
<th>$A_0 - A$</th>
<th>$A_0 - A_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>$4.990 \times 10^{-6}$</td>
<td>0.1781</td>
<td>29.107</td>
<td>-5.209</td>
<td>1.463</td>
</tr>
<tr>
<td>2</td>
<td>35</td>
<td>$1.791 \times 10^{-5}$</td>
<td>0.1729</td>
<td>9.530</td>
<td>-4.767</td>
<td>0.979</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>$2.912 \times 10^{-5}$</td>
<td>0.1708</td>
<td>7.346</td>
<td>-4.530</td>
<td>0.866</td>
</tr>
<tr>
<td>4</td>
<td>105</td>
<td>$4.889 \times 10^{-5}$</td>
<td>0.1667</td>
<td>4.936</td>
<td>-4.302</td>
<td>0.673</td>
</tr>
<tr>
<td>5</td>
<td>130</td>
<td>$6.100 \times 10^{-5}$</td>
<td>0.1645</td>
<td>4.140</td>
<td>-4.214</td>
<td>0.617</td>
</tr>
<tr>
<td>6</td>
<td>230</td>
<td>$1.031 \times 10^{-4}$</td>
<td>0.1571</td>
<td>2.540</td>
<td>-3.996</td>
<td>0.404</td>
</tr>
<tr>
<td>7</td>
<td>320</td>
<td>$1.416 \times 10^{-4}$</td>
<td>0.1502</td>
<td>1.745</td>
<td>-3.040</td>
<td>0.241</td>
</tr>
<tr>
<td>8</td>
<td>480</td>
<td>$1.935 \times 10^{-4}$</td>
<td>0.1404</td>
<td>1.084</td>
<td>-3.713</td>
<td>0.035</td>
</tr>
<tr>
<td>9</td>
<td>580</td>
<td>$2.248 \times 10^{-4}$</td>
<td>0.1351</td>
<td>0.840</td>
<td>-3.648</td>
<td>0.075</td>
</tr>
<tr>
<td>10</td>
<td>4000</td>
<td>$6.680 \times 10^{-4}$</td>
<td>0.0766</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Benzilmonoxime (10$^{-3}$ mol dm$^{-3}$ in acetonitrile) is added to an acetonitrile solution of copper(II) acetate (2ml, 10$^{-3}$ mol dm$^{-3}$)
concentration of added benzilmonoxime to the solution as the concentration of benzilmonoxime anion. Such assumption is valid under the circumstances of that one is aiming at the determination of the composition rather than the other thermodynamic parameters. For measuring the other thermodynamic parameters like equilibrium, one need to determine the concentration of benzilmonoxime in the solution accurately. Hence, observed method has limitation in finding out the thermodynamic parameters as the determination of exact concentrations of benzilmonoxime in the presence of other absorbing species is not possible by electronic spectroscopy under our reaction condition. A plot of log(BMO) vs log R gives linear plot with a slope of 0.85 (Fig. 2.2.9) and that the slope is equal to n suggests replacement of an acetate group. This is an equilibrium study purely based on assumption that dimeric copper(II) acetate core is remaining intact during the course of study. In fact, at higher concentration of BMO linear plot is not observed suggesting extensive degradation of the dimeric core. Similar study on the interaction of diacetylmonoxime
Fig. 2.2.9: Plot of log[BM0] vs. log R
(refer Table 2.2.3 & Equation 2.2.4)

\[\log R = n \log[BM0] + \log K\]
\[n = 0.85 \approx 1\]

Slope = 0.85
with copper(II) acetate also suggests analogous result. The original absorbance at 673 nm of a solution containing copper(II) acetate in acetonitrile decreases on addition of diacetylmonoxime and a new absorption maximum at 388 nm appears. An isobestic point at 565 nm is observed on gradual addition of diacetylmonoxide to a copper(II) acetate solution (Fig. 2.2.10). The following equation can satisfactorily explain the transformation taking place in solution (Equation 2.2.5).

\[
K_C
\]

\[
\text{Cu}_2(\text{OAc})_4 + n\text{DAMH} \rightleftharpoons \text{Cu}_2(\text{OAc})_{4-n} (\text{DAM})_n + n\text{AcOH}
\]

\[
K_C = \frac{[\text{Cu}_2(\text{OAc})_{4-n} (\text{DAM})_n ][\text{AcOH }]^n}{[\text{Cu}_2(\text{OAc})_4 ][\text{DAMH }]^n}
\]

Where,

DAMH = diacetylmonoxime

DAM = anion of diacetylmonoxime
Fig. 2.2.10: Isobestic point at 565 nm on gradual addition of diacetylmonoxime to copper(II) acetate solution in acetonitrile.
\[ \log R = \log K_c + n \log [\text{DAMH}] \]

Where,

\[ R = \frac{[\text{Cu}_2(\text{OAc})_4 - n (\text{DAM})_n][\text{AcOH}]^n}{[\text{Cu}_2(\text{OAc})_4]} \]

\[ \frac{A_C - A}{A_o - A_C} \]

Equation 2.2.5

\( A_C \) is the absorbance at a concentration, \( C \), of diacetylmonoxime in acetonitrile solution of copper(II) acetate, \( A_o \) is the absorbance of copper(II) acetate solution at the beginning and \( A \) is the final absorbance at 673 nm. Variation of absorbance at 673 nm with the increase of diacetylmonoxime concentration is shown in Table 2.2.4. A plot of \( \log [\text{DAMH}] \) vs \( \log R \) gives a straight line with slope 1.14. Since \( n \) is equal to the number of acetato ligand displaced, results support replacement of one acetate group from the dimeric core.

As pointed out earlier this equilibrium state is based on the assumption that dimeric copper(II) acetate core is remaining intact during the course of ligand substitution. Our result shows that this linear relationship is valid only in dilute solution (Fig. 2.2.11). However, fast degradation under aerobic
Table 2-2-4

Equilibrium study of diacetylmonoxime and copper(II) acetate in acetonitrile --- variation of absorbance at 673 nm versus diacetylmonoxime concentration*.

\( A_0 = \) Absorbance of copper(II) acetate alone = 0.1477

\( A = \) Final absorbance \((A_C) = 0.0491\)

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>Volume of DAMH added in microitre</th>
<th>Concentration of DAMH in mol dm(^{-3}) (C)</th>
<th>Absorbance (A_C)</th>
<th>(A_C - A)</th>
<th>(\log C)</th>
<th>(\log \frac{A_C - A}{A_0 - A})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>(9.90 \times 10^{-6})</td>
<td>0.1436</td>
<td>23.048</td>
<td>-5.004</td>
<td>1.360</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>(1.96 \times 10^{-5})</td>
<td>0.1406</td>
<td>12.880</td>
<td>-4.707</td>
<td>1.110</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>(2.912 \times 10^{-5})</td>
<td>0.1385</td>
<td>9.717</td>
<td>-4.537</td>
<td>0.987</td>
</tr>
<tr>
<td>4</td>
<td>80</td>
<td>(3.840 \times 10^{-5})</td>
<td>0.1352</td>
<td>6.888</td>
<td>-4.415</td>
<td>0.820</td>
</tr>
<tr>
<td>5</td>
<td>120</td>
<td>(5.660 \times 10^{-5})</td>
<td>0.1309</td>
<td>4.866</td>
<td>-4.247</td>
<td>0.697</td>
</tr>
<tr>
<td>6</td>
<td>160</td>
<td>(7.400 \times 10^{-5})</td>
<td>0.1253</td>
<td>3.401</td>
<td>-4.130</td>
<td>0.531</td>
</tr>
<tr>
<td>7</td>
<td>200</td>
<td>(9.090 \times 10^{-5})</td>
<td>0.1196</td>
<td>2.508</td>
<td>-3.941</td>
<td>0.399</td>
</tr>
<tr>
<td>8</td>
<td>250</td>
<td>(1.071 \times 10^{-4})</td>
<td>0.1153</td>
<td>2.048</td>
<td>-3.770</td>
<td>0.310</td>
</tr>
<tr>
<td>9</td>
<td>300</td>
<td>(1.304 \times 10^{-4})</td>
<td>0.1091</td>
<td>1.554</td>
<td>-3.584</td>
<td>0.191</td>
</tr>
<tr>
<td>10</td>
<td>420</td>
<td>(1.725 \times 10^{-4})</td>
<td>0.0997</td>
<td>0.927</td>
<td>-3.470</td>
<td>-0.032</td>
</tr>
<tr>
<td>11</td>
<td>900</td>
<td>(3.103 \times 10^{-4})</td>
<td>0.0491</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

* Diacetylmonoxime \((10^{-3} \text{ mol dm}^{-3} \text{ in acetonitrile})\) is added to an acetonitrile solution of copper(II) acetate \((2 \text{ ml}, 10^{-3} \text{ mol dm}^{-3})\).
Fig. 2.2.11: Plot of $\log[DAMH]$ vs. $\log R$
(refer Table 2.2.4 & Equation 2.2.5)

$log R = n \log[DAMH] + \log K$

$n = 1.14 \approx 1$

Slope = 1.14
Fig. 2.2.12: Fall in absorbance of copper(II)-diacetylmonoxime complex at 388 nm with time.
Table 2.2-4A

Absorbance of copper(II)-diacetylmonoxime complex (1.5065 x 10^{-3} mol dm^{-3} in acetonitrile) at 388 nm versus time.

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>Time in Minute</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.0799</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>0.0752</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>0.0720</td>
</tr>
<tr>
<td>4</td>
<td>13</td>
<td>0.0706</td>
</tr>
<tr>
<td>5</td>
<td>19</td>
<td>0.0703</td>
</tr>
<tr>
<td>6</td>
<td>25</td>
<td>0.0700</td>
</tr>
<tr>
<td>7</td>
<td>29</td>
<td>0.0690</td>
</tr>
<tr>
<td>8</td>
<td>32</td>
<td>0.0673</td>
</tr>
<tr>
<td>9</td>
<td>36</td>
<td>0.0671</td>
</tr>
<tr>
<td>10</td>
<td>40</td>
<td>0.0663</td>
</tr>
<tr>
<td>11</td>
<td>45</td>
<td>0.0656</td>
</tr>
<tr>
<td>12</td>
<td>50</td>
<td>0.0639</td>
</tr>
<tr>
<td>13</td>
<td>60</td>
<td>0.0575</td>
</tr>
<tr>
<td>14</td>
<td>70</td>
<td>0.0355</td>
</tr>
</tbody>
</table>
condition of the diacetylmonoxime complex is observed in solution. A plot of the reduction of absorbance at 388 nm vs time is shown in Fig. 2.2.12 (Table 2.2.4A).

These two sets of experiments suggest that in a dilute solution limit copper(II) acetate dimeric core may exchange one acetato group with the two 1,2-dione oximes namely benzilmonoxime and diacetylmonoxime.

2.2.3 INFRARED STUDY:

Infrared spectroscopy is a powerful technique for identifying functional groups. This is particularly true for functional groups like carbonyl, peroxo and hydroxyl group. Hence, a study aimed at distinguishing a few of the possible modes of co-ordination in copper(II) oxime complex with benzoyl peroxide is performed. Benzoyl peroxide has its C=O stretching frequency at 1756 cm\(^{-1}\) (Fig. 2.2.13B). Copper(II) acetate and benzophenone oxime do not absorb in this region. There is no new peak in the IR of a mixture of copper(II) acetate, benzoyl peroxide and benzophenone oxime (0.2:0.2:1 mole ratio) in nujol other than those of the constituents. When a drop of acetonitrile is added to this mixture two new peaks appear at 1718 and
Table 2.2.5
IR spectral study on interaction of benzoyl peroxide with Cu-oxime complex. Comparative statement of IR bands (in cm$^{-1}$) of single compounds and various mixtures in nujol.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Oxime (DO)</th>
<th>Peroxide</th>
<th>Cu(OAc)$_2$ BO</th>
<th>Cu(OAc)$_2$ + BP</th>
<th>Cu(OAc)$_2$</th>
<th>Cu(OAc)$_2$ + BP</th>
<th>Benzobenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>3470</td>
<td>2912</td>
<td>3472</td>
<td>3495</td>
<td>3420</td>
<td>3373</td>
<td>2920</td>
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</table>
IR OF Cu(OAc)$_2$ IN NUJOL

IR OF Cu(OAc)$_2$ + BENZOPHENONE OXIME IN NUJOL

IR OF BENZOPHENONE OXIME IN NUJOL

FIG. 2-2.13 A
FIG. 2-2.13 B
FIG 2.2.13C

IR of Cu(OAC)$_2$ + BENZOPHENONE OXIME + BENZOYLPEROXIDE + CH$_4$CH IN NUJOL

EXPANSION OF ABOVE IR
1704 cm$^{-1}$ (Table 2.2.5). This effect is attributed to the higher dielectric constant of acetonitrile than nujol in mixing the substrates uniformly. The IR spectra of a mixture of copper(II) acetate and benzoyl peroxide also do not show any change from the spectra of its constituents in both nujol as well as in acetonitrile. Appearance of the two new signals with lower frequency than the original C=O band of benzoyl peroxide suggest it to be co-ordinating through a chelating structure as shown in structures XXXIV, XXXV and XXXVI. To illustrate the effect the IR of each constituents along with different combinations are shown in Fig. 2.2.13A - C. The type of interaction shown in figure XXXV is preferred over that shown in XXXVI as the two new signals are observed. The type XXXIV interaction through the peroxy oxygen is ruled out as in such an interaction the carbonyl frequency would shift towards higher side.

2.2.4 KINETIC STUDY:

Kinetics of the reaction of benzilmonoxime with a mixture of copper(II) acetate and benzoyl
peroxide in acetonitrile as solvent has been studied with the help of visible spectroscopy. Change of absorption of the reaction mixture at 418 nm with time is an indication of the progress of the reaction. A few representative plots are shown in Fig. 2.2.14 - 18. As the reaction proceeds the absorption initially decreases and then increases linearly for some time. The kinetic data supports the following formulation:

\[ \text{Equation 2-2.6} \]

Let \([\text{Cu}_2(\text{OAc})_4 - n(\text{BMA})_n] = A\) and adduct of A with BP = B and assuming \(k_{-1}\) as small.
Let \( \frac{d[A]}{dt} = k_1[A] \)

\[ \Rightarrow - \frac{d[A]}{[A]} = k_1 dt \]

\[ \Rightarrow \ln \frac{[A]}{[A_0]} = -k_1 t, \text{ where } [A] = [A_0] \text{ at } t = 0 \]

\[ \Rightarrow [A] = [A_0] e^{-k_1 t} \]

\[ \Rightarrow \frac{d[B]}{dt} = k_1[A] - k_2[B] \]

\[ = k_1[A_0] e^{-k_1 t} - k_2[B] \]

\[ \Rightarrow \frac{d[B]}{dt} + k_2[B] = k_1[A_0] e^{-k_1 t} \]

Let \( k_1[A_0] = k'_1 \)

Then,

\[ \frac{d[B]}{dt} + k_2[B] = k'_1 e^{-k_1 t} \]

Integrating factor = \( e^{\int k_2 dt} = e^{k_2 t} \)

\[ [B]e^{k_2 t} = \int k'_1 e^{-k_1 t} e^{k_2 t} dt \]

\[ = k'_1 \int e^{(k_2 - k_1) t} dt \]
\[ \Rightarrow \quad [B]e^{k_2 t} = \frac{k_1' e^{(k_2 - k_1)t}}{k_2 - k_1} + C \]

when \( t=0, [B]=0 \)
\[ C = \frac{-k_1'}{k_2 - k_1} \]

\[ [B]e^{k_2 t} = \frac{k_1'}{k_2 - k_1} \left( e^{(k_2 - k_1)t} - 1 \right) \]

\[ \Rightarrow \quad [B] = \frac{k_1'}{k_2 - k_1} [ e^{-k_1 t} - e^{-k_2 t} ] \]

\[ \Rightarrow \quad [B] = \frac{k_1[A_0]}{k_2 - k_1} [ e^{-k_1 t} - e^{-k_2 t} ] \]

Since \( k_1 \) and \( k_2 \) are small quantities

\[ [B] = \frac{k_1[A_0]}{k_2 - k_1} \left[ 1 - k_1 t - 1 + k_2 t \right] \]

\[ \Rightarrow \quad [B] = k_1[A_0] t \]

\[ \Rightarrow \quad [B] \propto t \]

A plot of \([B]\) against time gives a straight line with slope equal to \( k_1[A_0] \). Several \( k_1 \) values obtained from
Fig. 2.2.14: Absorbance vs. time plot for a mixture of copper(II) acetate, benzoyl peroxide and benzilmonoxime at 418 nm.

Absorbance Copper(II) acetate : BP : BMO = 1 : 1 : 5
Fig. 2.2.15: Absorbance vs. time plot for a mixture of copper(II) acetate, benzoyl peroxide and benzilmonoxime in acetonitrile at 418 nm.

Absorbance  Copper(II) acetate : BP : BMO = 1 : 2 : 5
Fig. 2.2.16: Absorbance vs. time plot for a mixture of copper(II) acetate, benzoyl peroxide and benzilmonoxime in acetonitrile at 418 nm.

Copper(II) acetate : BP : BMO = 1 : 3 : 5

Slope = 3.3 \times 10^{-5}
Fig. 2.2.17: Absorbance vs. time plot for a mixture of copper(II) acetate, benzoyl peroxide and benzilmonoxime in acetonitrile at 418 nm.

Copper(II) acetate : BP : BMO = 1 : 5 : 5

Absorbance

Slope = $3.4 \times 10^{-5}$

--- Time in minute ---
Fig. 2.2.18: Absorbance vs. time plot for a mixture of copper(II) acetate, benzoyl peroxide and benzilmonoxime in acetonitrile at 418 nm.

Copper(II) acetate : BP : BMO = 1 : 5.5 : 5

Absorbance

Slope = 3.4 \times 10^{-5}
variation of the concentration of benzoyl peroxide under pseudo first order conditions are tabulated in Table 2.2.6. The absorbance of the reaction mixtures with different concentrations of benzoyl peroxide are recorded in Tables 2.2.7 to 2.2.11.

Feasibility of the complex of the type B (Equation 2.2.6) is supported by earlier work of Christou et al.\textsuperscript{122} where dimeric complex of copper(II) with acetate as bridging groups are reported and also from the fact that dimeric copper(II) complexes are relatively easy to prepare from dimeric precursors\textsuperscript{132}. Visible spectroscopic study (Section 2.2.2) supports the formation of such a complex in solution.

Although the dimeric structure is over emphasised the kinetic study performed with copper(II) chloride have also shown results similar to the copper(II) acetate system as described above. A solution containing copper(II) chloride has a absorbance maximum at 464 nm. This absorbance decreases with time exponentially in absence of benzoyl peroxide (Fig. 2.2.19, Table 2.2.12). However, the reverse phenomenon takes place on addition of benzoyl peroxide (Fig. 2.2.20, Table 2.2.13).
Table 2.2.6

The observed rate constant, $k_1$, of the reaction of benzilmonoxime under pseudo first order condition with a mixture of copper(II) acetate and benzoyl peroxide at different concentration of benzoyl peroxide.

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>Ratio of copper(II) acetate : Benzilmonoxime : Benzoyl peroxide</th>
<th>$k_1$ in sec$^{-1}$</th>
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<tr>
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<td>1 : 5 : 3.5</td>
<td>$3.3 \times 10^{-2}$</td>
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<tr>
<td>2</td>
<td>1 : 5 : 4.7</td>
<td>$3.4 \times 10^{-2}$</td>
</tr>
<tr>
<td>3</td>
<td>1 : 5 : 5.5</td>
<td>$3.4 \times 10^{-2}$</td>
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</table>
Table 2.2.7
Absorbance of a mixture* of copper(II) acetate, benzoyl peroxide and benzilmonoxime in acetonitrile at 418 nm.

\[ \text{Cu(OAc)}_2 : \text{BP} : \text{BMO} = 1 : 1 : 5 \]

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* 0.0019 g (1 x 10^{-3} \text{ mol dm}^{-3}) \text{Cu(OAc)}_2 \cdot 2\text{H}_2\text{O} is dissolved in 10 ml of UV-grade CH$_3$CN. To 2 ml of this solution 0.0022 g (5 x 10^{-3} \text{ mol dm}^{-3}) of benzilmonoxime (BMO) and 0.0005 g (1\times10^{-3} \text{ mol dm}^{-3}) of benzoyl peroxide are added and dissolved. UV measurement is followed immediately.
Table 2.2.8
Absorbance of a mixture* of copper(II) acetate, benzoyl peroxide and benzilmonoxime in acetonitrile at 418 nm.

\[
\text{Cu(OAc)}_2 \text{ : BP : BMO} = 1 : 2 : 5
\]

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* Procedure is same as in Table 2.2.7.

BP = 0.0010 g (2 × 10⁻³ mol dm⁻³).
Table 2.2.9
Absorbance of a mixture* of copper(II) acetate, benzoyl peroxide and benzilmonoxime in acetonitrile at 418 nm.

Cu(OAc)$_2$ : BP : BMO = 1 : 3 : 5

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* Procedure is same as in Table 2.2.7.

BP = 0.0014 g ( 3 X 10$^{-3}$ mol dm$^{-3}$ ).
**Table 2.2.10**

Absorbance of a mixture* of copper(II) acetate, benzoyl peroxide and benzilmonoxime in acetonitrile at 418 nm.

Cu(OAc)$_2$ : BP : BMO = 1 : 4.7 : 5

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</table>

* Procedure is same as in Table 2.2.7.

BP = 0.0023 g (4.7 x 10$^{-3}$ mol dm$^{-3}$).
Table 2.2.11

Absorbance of a mixture* of copper(II) acetate, benzoyl peroxide and benzilmonoxime in acetonitrile at 418 nm.

\[ \text{Cu(OAc)}_2 : \text{BP} : \text{BMO} = 1 : 5.5 : 5 \]

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</table>

* Procedure is same as in Table 2.2.7.

\[ \text{BP} = 0.0026 \text{ g (5.5 } \times 10^{-3} \text{ mol dm}^{-3}) \].
Fig. 2.2.19: Absorbance vs. time plot for a mixture of copper(II) chloride and benzilmonoxime in acetonitrile at 464 nm.
Copper(II) chloride : BMO = 1 : 5
**Table 2.2.12**

Absorbance of a mixture* of copper(II) chloride and benzilmonoxime in acetonitrile at 464 nm.

\[
\text{CuCl}_{2} \text{ : BMO = 1 : 5}
\]

<table>
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<tr>
<td>11</td>
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* 0.0017 g (1 x 10^{-3} mol dm^{-3}) CuCl_{2}.2H_{2}O is dissolved in 10 ml of UV-grade CH_{3}CN. To 2 ml of this solution 0.0022 g (5 x 10^{-3} mol dm^{-3}) of benzilmonoxime (BMD) is added and dissolved. UV measurement is followed immediately.
Fig. 2.2.20: Absorbance vs. time plot for a mixture of copper(II) chloride, benzoyl peroxide and benzilmonoxime in acetonitrile at 464 nm.

Copper(II) chloride : BP : BMO = 1 : 1 : 5
Table 2.2.13

Absorbance of a mixture* of copper(II) chloride, benzilmonoxime and benzoyl peroxide in acetonitrile at 464 nm.

\[ \text{CuCl}_2 : \text{BMO} : \text{BP} = 1 : 5 : 1 \]

<table>
<thead>
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<th>Entry No.</th>
<th>Time in Minute</th>
<th>Absorbance</th>
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</table>

* Procedure is same as in Table 2.2.12.

BP = 0.0005 g (1 x 10^{-3} mol dm^{-3}).
2.2.5 PROBABLE MECHANISM:

From the above discussions the mechanisms shown in Scheme III and Scheme IV may be proposed. The mechanism in Scheme III is ruled out as it cannot explain the product formation such as amides. However, this mechanism predominates in Mn-catalysed reactions\textsuperscript{133}. The kinetic study and the observations such as that, the reactions do not proceed in presence of radical scavengers and in protic medium the mechanism shown in Scheme IV is favoured. The additional support to this mechanism comes from the fact that the reactions can be performed by the use of a mixture of anhydrous CuCl\textsubscript{2} and benzoyl peroxide in anhydrous condition. It has not been possible to observe the e.s.r. signals of radicals from solution of copper(II) acetate, benzophenone oxime and benzoyl peroxide. A broad signal with g value at 3330 G is observed.
SCHEME III

\[ \text{Ph} \quad \text{BzO} \quad \text{Cu(II)(Oxime)}_n \quad \rightarrow \quad [\text{Cu(III)(OBz)(Oxime)}_n] \]

\[ \text{[Cu(Oxime)}_n^{2+} + \cdot\text{OBz} \quad \quad \rightarrow \quad \text{R}^1 \quad \text{R}^2 \quad \text{NOBz} \quad \rightarrow \quad \text{R}^1 \quad \text{C} \equiv \text{N} \quad \text{O} \quad \text{R}^1 \quad \text{NH}_2 \]

SCHEME IV