

Role of mixed ligand Pd(II) and Pt(II) complexes in photooxygenation reaction

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Abstract: Mixed ligand complexes of the formula $[M(\text{phen})\text{bdt}]$ where $M = \text{Pd(II)}$ or Pt(II) , $\text{phen} = 1,10\text{-phenanthroline}$ and $\text{bdt} = 1,2\text{-benzenedithiolate}$ have been synthesized and studied as photosensitizers of singlet molecular oxygen ($^1\text{O}_2$) production. It was observed that, Pt(II) complex shows a better photosensitizing ability as compared to its Pd(II) analogue. However, both Pd(II) and Pt(II) complexes act as chemical quenchers of $^1\text{O}_2$, resulting in their photooxidation shown by decay of the respective complex. Thus Pt(II) complex undergoes selfsensitized photooxidation by $^1\text{O}_2$. The solvent dependence of this reaction is undertaken by performing the experiment using pure DMF (dimethyl formamide) and 10% H_2O in DMF as solvent. The comparison of rate of decay of the Pt(II) and Pd(II) complexes show enhancement of the reaction in presence of water. The decay of the complex was monitored by recording the difference absorption spectra of the complex in the visible region after definite irradiation times. Involvement of $^1\text{O}_2$ is further supported by quenching studies of this reaction using NaN_3 as physical quencher of $^1\text{O}_2$.

Key words: chemical quenching, photooxygenation reaction, photosensitizer, photooxidation, singlet oxygen

I. Introduction:

Photochemistry plays an important role in producing chemical compounds or bringing them into reaction. The development of chelating ligands and their transition metal complexes has been of increasing interest. Square-planar Pt(II) , Pd(II) , and Au(III) terpyridine complexes show their potential as antitumor and antiprotozoal agents. Photosensitization is an important photochemical reaction involving generation and quenching of singlet molecular oxygen ($^1\text{O}_2$), which is one of the most active intermediates in chemical and biochemical reactions[1].

The study of singlet molecular oxygen production and reactivity has emerged as a rich and diverse area with implications in various fields. It has a characteristic chemistry that sets it apart from the triplet ground state of molecular oxygen ($^3\text{O}_2$) and is important in fields that range from atmospheric chemistry and material science to biology and medicine[2]. It is found to play major role in photodynamic effect. Application of this effect to blood sterilization, cancer therapy, and insecticides, pesticides is of increasing importance. The literature has offered new data related to its application in wastewater treatment[3]. Therefore study of generation and quenching of singlet oxygen becomes important. It has been demonstrated that Pt(II) and Pd(II) diimine complexes sensitize the formation of singlet oxygen ($^1\text{O}_2$) from ground state molecular oxygen ($^3\text{O}_2$). Photosensitizing ability of Ru(II) complexes has also been studied. Ni(II) complexes have been reported to be quenchers of singlet oxygen[4-6].

$[\text{Pd}(\text{phen})\text{DMT}]$ has been reported as acceptor (chemical quencher) of singlet molecular oxygen whereas the analogous Pt(II) complexes have shown to undergo self-sensitized photooxidation [7].

II. Experimental:

2.1 Materials and equipments:

The chemicals used for the present study, potassium tetrachloroplatinate [K_2PtCl_4] (sd-Fine), PdCl_2 (Sigma Aldrich), 1,2-benzenedithiol(bdt) (Aldrich) & 1,10 phenanthroline (phen), Sodium azide (NaN_3), Hematoporphyrin, Dimethylformamide (DMF), Dimethylsulphoxide (DMSO), Chloroform and Acetone were purchased from SISCO. Microprocessor photocolormeter (Esico model-1313) and Double Beam UV/VIS Spectrophotometer (Systronics-Model AU- 2700/2701) was used to measure absorbance before and after irradiation. Tungsten-Halogen lamp (300W) was used for irradiation purpose. A transparent colourless acrylic box (21.5 cm \times 11.5 cm \times 11.5 cm) was used as heat filter to prevent the sample solution from getting heated.

2.2 Synthetic work:

$[\text{M}(\text{phen})\text{bdt}]$: Mixed ligand complexes of the type $[\text{M}(\text{phen})\text{bdt}]$ where $M = \text{Pd(II)}$ or Pt(II) have been synthesized by the procedure reported in the literature [6,8].

2.3. General Irradiation Procedure:

For irradiation, a wooden box (75 cm × 25 cm × 19 cm) was used as a dark chamber. At one end of this wooden box, the light source was fitted. The acrylic box was placed at a fixed distance (15 cm) from the source. The solution to be photolyzed was transferred into a cuvette having 1 cm path length and was placed at the other side of the acrylic box (at a distance of 6 cm) for irradiation. Absorbance of this solution was measured before and after irradiation.

2.4 Photochemical Studies:

A 0.2mM solution of [M(phen)(bdt)] in DMF was bubbled with molecular oxygen for 20 minutes. It was irradiated for different time intervals and absorbance of the solution was measured as a function of time. Taking into account the difference in behaviour, separate experiments were performed for Pd(II) and Pt(II) complexes.

2.4.1 [Pt(phen)(bdt)] :

Photolysis of [Pt(phen)(bdt)] was performed with and without sodium azide, a well known Physical quencher of 1O_2 . For this, pilot experiments were performed with different concentrations of the complex and NaN_3 to select optimum concentration range. Oxygen saturated solution of [Pt(phen)bdt] (0.2mM) and different concentrations of NaN_3 (0, 0.05mM and 0.1mM) was irradiated and decay of the complex was monitored by noting the absorbance after definite irradiation times. Photolysis of molecular nitrogen saturated solution of the complex was also studied.

2.4.2 [Pd(phen)(bdt)] :

After a series of pilot experiments the optimum concentration of solution to be photolyzed was decided. Photolysis of [Pd(phen)bdt] (0.5mM), Hematoporphyrin (0.08mM) and sodium azide (0.05mM) was carried out. A parallel experiment was also performed in absence of sodium azide for comparison. Pure oxygen gas was bubbled through the solutions for 15 minutes before irradiation. Similar experiment was performed after passing molecular nitrogen through the experimental solution.

2.4.3. Solvent Effect:

Photolysis of the complex has been performed using 10 % aqueous DMF to study the effect of solvent. The reaction was monitored by recording difference absorption spectra after definite time intervals.

III. Results and Discussion:

The complexes were characterized by IR and NMR. The spectra obtained are in good agreement with those reported in the literature [9-11]. The [M(phen)bdt] complexes show five absorption bands. The lowest triplet state 3S_1 of the longest wavelength is photochemically important as shown earlier in [Pd(bpy)(dmt)].

3.1 Photochemical studies:

3.1.1 [Pd(phen)bdt] as an acceptor of 1O_2 :

Absorbance of Oxygen saturated solution containing 0.5mM [Pd(phen)bdt] and 0.08mM Hematoporphyrin at 500nm was found to decrease which may be due to the decay of [Pd(phen)bdt] complex. However, when the mixture was irradiated in presence of pure molecular nitrogen, this decay was not observed. Also, there was no decrease in absorbance if the solution was kept in dark. There was 5% decrease in absorbance when oxygen saturated solution of [Pd(phen)bdt] was irradiated for 4 hours. Therefore it can be concluded that the decrease in absorbance is due to the combined action of the complex [M(phen)bdt], Hematoporphyrin, light and molecular oxygen. Hematoporphyrin is a well-known sensitizer of 1O_2 . Therefore this decay might involve singlet molecular oxygen (fig.1). Involvement of singlet oxygen is proved by quenching of this decay in presence of sodium azide.

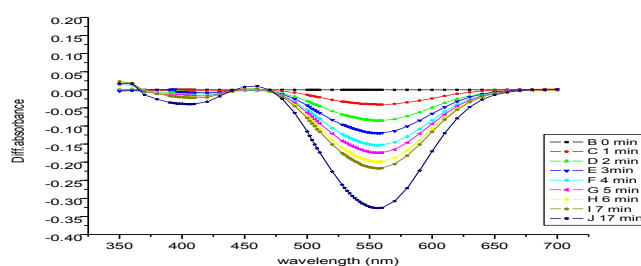
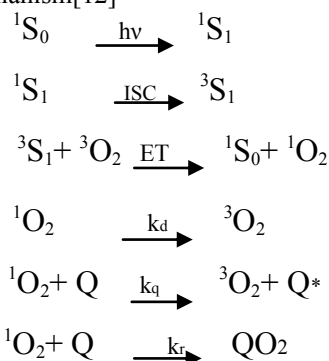


Fig 1: Decay of the complex on irradiation in presence of hematoporphyrin

From the above results, it can be noted that Pd(II) complex under study acts as chemical quencher of $^1\text{O}_2$. This can be explained by the following mechanism[12]-



S = Hematoporphyrin

Q = [Pd(phen)bdt]

3.2.1. Self-sensitized photooxidation of [Pt(phen)bdt]:

Oxygen saturated solution of [Pt(phen)bdt] (0.2mM) in DMF was irradiated with visible radiation . The absorbance was noted at different times of irradiation to study the photolysis. The photolysis results in decay of the complex which is shown by decrease in absorbance of the solution. The change in absorbance corresponds to the amount reacted(x) and initial absorbance is taken as “a”. A graph is plotted between (x/a-x) of the complex vs. irradiation time (Fig:2.1 and 2.2).

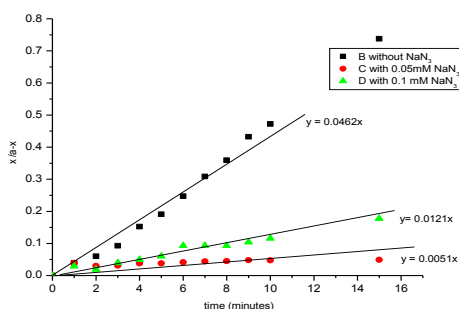


Fig.2.1 plot of (x/a-x) of the complex [Pt(phen)(bdt)] and different concentrations of sodium azide against time

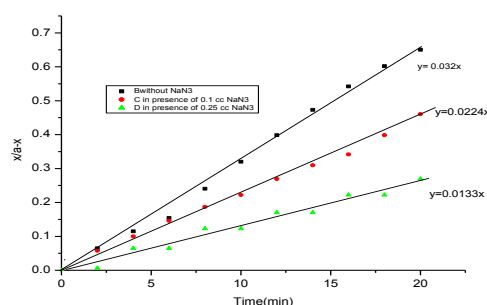


Fig.2.2: plot of (x/a-x) of the complex [Pd(phen)(bdt)] and different concentrations of sodium azide against time

Linear nature of the plot indicates that the decay of [M(phen)bdt] follows second order kinetics. This is also confirmed by log-log plot .This photolysis was further studied in presence of known $^1\text{O}_2$ quencher such as sodium azide(NaN_3). It was found that the decay of the complex was reduced when NaN_3 was added to [Pt(phen)bdt] and then irradiated. Oxygen saturated solution of [Pt(phen)bdt] (0.2mM) and NaN_3 (0.1mM) was irradiated and decay of the complex was monitored by noting the absorbance after definite irradiation times. It can be seen from Fig.1 that when concentration of NaN_3 is increased, decay of the complex is reduced. A comparison of the slopes of lines confirms this trend. A remarkable change in the color of the oxygen saturated solution of [Pt(phen)bdt] in DMF was observed before and after irradiation. Reddish purple color of the solution before irradiation changed to pale yellow after irradiation for thirty minutes. This may be due to a chemical reaction between [Pt(phen)bdt] and $^1\text{O}_2$ produced during photolysis. Quenching of this reaction in presence of NaN_3 , indicates the involvement of singlet oxygen. This was further confirmed by the fact that there was no decrease in absorbance on photolysis in presence of pure molecular nitrogen. Also, if this solution was kept in dark, no decrease in absorbance was observed. Thus it can be concluded that the above decay requires combined action of [Pt(phen)bdt], light and oxygen. This indicates that the complex acts as photosensitizer as well as acceptor of singlet oxygen. The process is thus referred to as self sensitized photooxidation. The mechanism proposed for this reaction is similar to that explained earlier for [Pt(phen)DMT] and [Pt(phen)TSA] [12]. Mixed ligand complexes containing 1,10-phenanthroline as one of the ligands and catechol or tertiary butyl catechol as the other have also been reported to be stable to light irradiation for 5-6 hours . This confirms that it is not the phenanthroline moiety in [Pt(phen)bdt] which is attacked during photooxidation[7]. Thus it can be concluded that it must be the 1,2- benzenedithiol moiety which is attacked by $^1\text{O}_2$. This is supported by the literature which reveals the interaction of thioethers with $^1\text{O}_2$ to give sulphoxides . Also it has been shown that [Pt(bpy)bdt] where bpy= 2,2' bipyridine can quench $^1\text{O}_2$ to form sulphonated products[8].

The $^1\text{O}_2$ production by the [M(phen)bdt] complex depends on the ligand field splitting by the ligands attached to the metal. But in this case, as both ligands are same, we consider the metal. In Pt(II), the ligand field

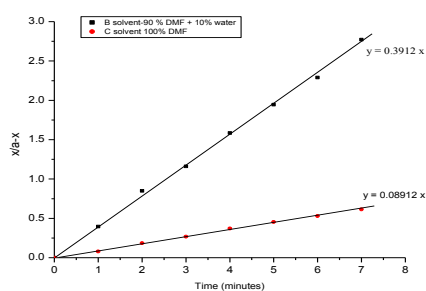
increases by 30% to 50% from the corresponding Pd(II) complexes. Therefore the 3A_2 state has much higher energy with respect to 3S_1 . Thus Pt(II) complexes are better sensitizers. However in [Pd(phen)bdt], they may have the 3A_2 state just below the 3S_1 which provides pathway of radiationless decay resulting in its decreased photosensitizing ability.

3.2.2 Photooxygenation of complexes in mixed solvent:

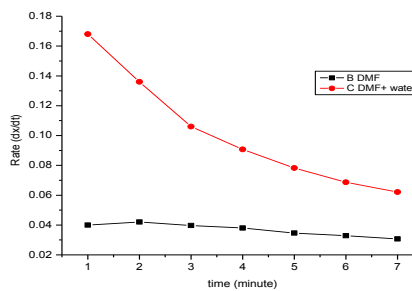
Review of literature reveals that reaction of metal thiolato complex with singlet oxygen can lead to several products [9-11] as -

- i. Formation of sulfenate at one of the sulfur sites only.
- ii. Formation of a bis-sulfenate.
- iii. Formation of mono or bisulfinate.
- iv. Formation of a mixed sulfenato/sulfinato complex.

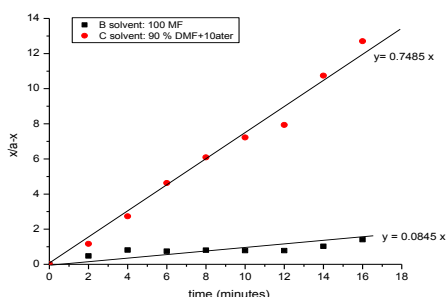
In Co(III) thiolato complexes it has been reported earlier that protic solvents decrease the susceptibility of the thiolate ligand toward attack by singlet oxygen, but greatly increase the conversion of the peroxidic intermediate to the sulfenato product [13,14].



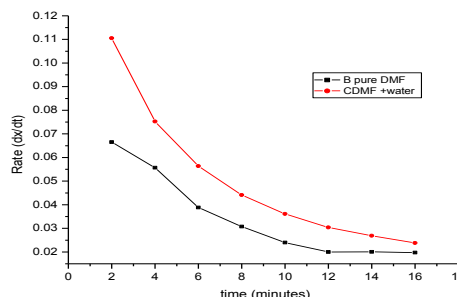
3.1a



3.2a



3.1b



3.2b

Fig 3.1a &b: Plot of (x/a-x) against time

Fig 3.2a&b: Plot of rate against time

Fig 3.1 a &b: the second order plots of [Pt(phen)(bdt)] and [Pd(phen)(bdt)]. The comparison of slopes of the lines suggests the enhancement in reaction in presence of aqueous (10% water in DMF) solvent. Fig 3.2 a &b: The plot of rate (dx/dt) against time shows increase in rate of photolysis of the complexes. Higher rate of reaction may be due to stabilisation of reaction intermediate in presence of water (protic solvent) [14].

IV. Conclusion:

Comparative study of [M(phen)(bdt)] shows that [Pt(phen)(bdt)] acts as photosensitizer as well as acceptor (chemical quencher) of 1O_2 whereas [Pd(phen)(bdt)] although not a photosensitizer, acts as chemical quencher of 1O_2 . The observations suggest an increase in the reaction rate when the solvent DMF contains 10% water. This may be due to the stabilization of the intermediate in presence of water. It has been reported recently that mixed ligand Pd(II) complexes exhibit significant biological activity [15]. Thus, in future, these complexes can be tested for their biological activity.

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