

Kinetics of photo-oxidation of Pd(II) complexes with Thiosalicylic acid and 1,10-phenanthroline

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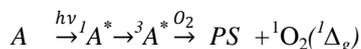
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Abstract: The complexes of the formula $[Pd(phen)(tsa)]$ and $[Pd(tsa)_2]$ (where phen = 1,10-phenanthroline and tsa = dianion of thiosalicylic acid) were synthesized replacing solvent DMSO by water, in order to develop a cleaner chemical synthetic process. Photosensitivity of the synthesized complexes has been studied. A series of photochemical experiments has been performed to investigate the role of these complexes in photo-oxygenation reactions. Study of photolysis of these complexes suggests the involvement of singlet oxygen which is further confirmed by using sodium azide as quencher of 1O_2 . Progress of the reaction is monitored by UV-visible spectrophotometry. The rate constant and yield of singlet oxygen has been determined using DPBF(1,3-diphenylisobenzofuran) as probe. It has been observed that the type of solvent used in synthesis does not affect its photochemical behavior which encourages the use of greener solvent like H_2O for synthetic purposes. These Pd(II) complexes act as chemical quenchers of singlet oxygen and undergo self-sensitized photo-oxidation. The photochemical behavior of these complexes can be exploited for biological application as Pd(II) complexes are biologically active.

Keywords: Pd (II) complex, Singlet oxygen, Photolysis, DPBF, Quencher.

I. Introduction

Transition metal complexes in excited state undergo a number of different chemical reactions, most of which involve photochemical pathway. Absorption of light in the ultra-violet, visible or near IR regions of the spectrum by a co-ordination complex substrate (A) of the general formula $[ML]$ (where M-metal centre, L-ligand) results in generation of electronically excited state. The subsequent rapid passage of the system along deactivation routes leads to the eventual formation of relatively long lived lowest excited state of the substrate (A^*).



Depending on the co-ordination complex involved (A^*) can be charge transfer (metal to ligand, ligand to metal, complex to solvent), metal centered or ligand localized in nature. It is more energetic and exhibit different patterns of reactivity. These reactive pathways are kinetically competitive with radiative and non-radiative modes of decay[1]. In non-radiative decay, detection of singlet molecular oxygen (1O_2) can be accomplished through alternative technique such as monitoring the absorption of A^* excited substrate[2].

The study of generation and application of 1O_2 is important in various fields ranging from polymer science to cancer therapy. Srivastava *et al* reported Pt (II) and Pd(II) complexes as to undergo self-sensitized photo-oxidation and Ni (II) complexes as quenchers of singlet oxygen[3,4]. Luminescent Ru (II), Pt(II) Pd(II), Ir(III), Rh(III) complexes possess tuneable properties through ligand substitution that may offer photosensitization and photostability advantages. These complexes find applications in various fields including the ability to photosensitize the generation of singlet molecular oxygen (1O_2)[8].

A simple clean and controllable method for generation of singlet oxygen is photosensitization. The kinetics of singlet oxygen reactions with targets can be described in terms of total rate constant (k_t) that includes both physical and chemical reaction channels. Overall rate constant ($k_r + k_q$) have been determined for thousands of compounds. Determination of chemical reaction rate constant and quantum yield of singlet oxygen production normally involves the determination of substrate (A) consumption rate in steady state experiments and comparison with consumption rate of an actinometer[13-14].

In the present work Pd(II) complexes with 1-10,phenanthroline and thiosalicylic acid have been synthesized by the reported method and by using water as medium for synthesis. Structure confirmation is done by spectroscopic data and elemental analysis. The photochemical behavior is studied and quantum yield and rate constant have been determined [14].

II. Experimental

2.1: Materials and Equipment:

Palladium Chloride (PdCl_2), Thiosalicylic acid (2-mercaptobenzoic acid) (tsa), (Aldrich) & 1,10 phenanthroline (phen), Sodium azide (NaN_3), Hematoporphyrin DPBF (1,3-Diphenylisobenzofuran) (Sigma Aldrich), Dimethylformamide (DMF), Dimethylsulphoxide (DMSO) Anthracene (An) (Lobachemie), Chloroform and Acetone were purchased from SISCO.

UV-visible spectrophotometer (model -1313) 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: Synthesis

2.2.1 Complex I- $[\text{Pd}(\text{phen})(\text{tsa})]\cdot\text{H}_2\text{O}$

The complex has been synthesized by reported procedure using DMSO as solvent [4]. This complex has also been synthesized by replacing DMSO by water as solvent

Using water as solvent

PdCl_2 (1 mM) + 2.68 g NaCl dissolved in water (with stirring). TSA (1 mM in 2 cm³ of 1M NaOH and water) was then added to above solution with stirring followed by dropwise addition of 1,10 phenanthroline (1 mM) dissolved in methanol. Reddish orange precipitate of the complex $[\text{Pd}(\text{phen})(\text{tsa})]$ was obtained [8]. Kept overnight and then filtered and washed with water and acetone and dried to get red orange colored crystals of $[\text{Pd}(\text{phen})(\text{tsa})]\cdot\text{H}_2\text{O}$

2.2.2: Complex II- $[\text{Pd}(\text{tsa})_2]\cdot 2\text{H}_2\text{O}$

PdCl_2 (1 mM) + 2.68 g NaCl dissolved in acidified water (with stirring). TSA (2 mM in 4 cm³ of 1M NaOH and water) was then added to above solution with stirring. Blood orange colored precipitate obtained was allowed to settle overnight. The product was refluxed in ethanol, recrystallized and then used for photochemical analysis

2.3: Photochemical studies

To study the role of these complexes in photo-oxygenation reaction, various experiments were carried out

- The uv-visible spectra of the complexes were recorded in different solvents.
- Photolysis of the complexes in i) oxygen saturated solution ii) Nitrogen saturated solution iii) in presence of sensitizer (hematoporphyrin, anthracene) and iv) sodium azide for the confirmation of involvement of singlet oxygen.
- Determination of yield of singlet oxygen produced and the measurement of rate of reaction between singlet oxygen and given substrate.

2.3.1: General Irradiation Procedure:

A wooden box (75 cm \times 25 cm \times 19 cm) was used as a dark chamber for irradiation. At one end of this wooden box, the light source was fitted. The acrylic box was placed at a fixed distance from the source. The progress of reaction was followed by measuring absorbance after definite time intervals

Among the various methods for detecting the electronically excited molecule as reactive intermediate, chemical trapping and oxygen consumption is the most suitable method. We have selected chemical trapping using 1,3-diphenylisobenzofuran [12-14] as probe and the progress of the reaction is monitored by spectrophotometer by measuring the decrease in absorbance as a function of irradiation time at 415 nm.

2.3.2: Determination of quantum yield of singlet oxygen produced:

For the determination of quantum yield of the reaction, a comparative actinometry has been carried out with a standard photosensitizer and is optically matched with the sample. DPBF (chemical quencher of $^1\text{O}_2$) 77.6 μM , was used as probe, Anthracene (0.1 μM), Hematoporphyrin (0.1 μM) were used as sensitizers, 1 mM solution of the complexes (I & II) as the substrate. Dimethylformamide (DMF) was used as solvent. A loss in absorbance ($-\Delta A$) at 415 nm is determined after irradiation at definite time intervals.

2.3.2: Determination of rate constant of reaction between singlet oxygen and complex (k_r):

For determination of rate constant of reaction between $^1\text{O}_2$ and substrate (Pd(II) complex) the above experiment has been carried out for different substrate concentrations.

2.3.3: Kinetics of photo-oxidation and effect of aqueous solvent on rate of photo-oxidation:

To study the effect of mixed solvent on rate of photo-oxidation of the complexes, the reaction rates in pure DMF and 10% aqueous DMF were compared.

III. Results and Discussion

3.1 Characterization

Complex I-[Pd(phen)(tsa)].H₂O and Complex II- [Pd (tsa)₂].2H₂O

The **molar conductance** value of the 1 mM complex in DMF are complex I - 4.8 cm²ohm⁻¹mol⁻¹ and for complex II- 4.2 cm²ohm⁻¹mol⁻¹ respectively. This indicates the non-electrolytic nature of these complexes [16].

IR spectra have been recorded in the range 4000 to 200 cm⁻¹. The spectral change in the ligand moiety of complexes suggests the co-ordination of ligand to metal ion. IR ν_{max}/cm⁻¹ For complex I 3444(-O-H), 1255(-C-N), 1527(coordinated phenanthroline) and 1620 /1676 (-COO), 737(-Pd-S) for complex I and II, The IR band at 2520(S-H) cm⁻¹ in thiosalicylic acid is not present in both the complexes, suggesting binding of the ligand with metal.

Elemental Analysis

Complex I [C₁₉H₁₄O₃N₂PdS] –

Found: C, 49.79 ; H, 2.91; N, 6.73 ; S, 6.24 % Calculated: C, 49.91; H, 2.63 ; N, 7.0 ; S, 6.13%

Complex II [C₁₄H₁₂O₆PdS₂]-

Found: C, 37.63 ; H, 2.69 ; S, 14.34 % Calculated: C, 37.81; H, 2.63 ; S, 14.13 %

The spectroscopic data and elemental analysis data confirms the formation of both complexes.

3.2: The electronic absorption band maxima and the extinction coefficient:

Complex I – λ_{max} (DMF)/nm 430 (ε/dm³mol⁻¹cm⁻¹ 1500) 354 (4400), 335 sh(4150), 290 (14000), 276 (24000).

Complex II – λ_{max} (DMF)/nm 442 (ε/dm³mol⁻¹cm⁻¹ 2730), 373 (2940), 331 sh(2280)

The band at 430 nm in [Pd(phen)(tsa)] is solvent dependent. They experience a bathochromic shift with decrease in polarity of solvents from DMF to chloroform 30 nm shift in [Pd(phen)(tsa)]. This is attributed to charge transfer from highest occupied molecular orbital of TSA to the lowest unoccupied molecular orbital of 1,10-Phenanthroline ligand via metal [4-7]

3.3: Direct Photolysis:

Photochemical reactions that result from uptake of solar quanta directly by a substrate (followed by rearrangements or other reactions of the excited state) is referred to as direct photolysis. The complexes (1 mM, air saturated solution in DMF) under investigation undergo photolysis as shown in the Fig:1(a & b)

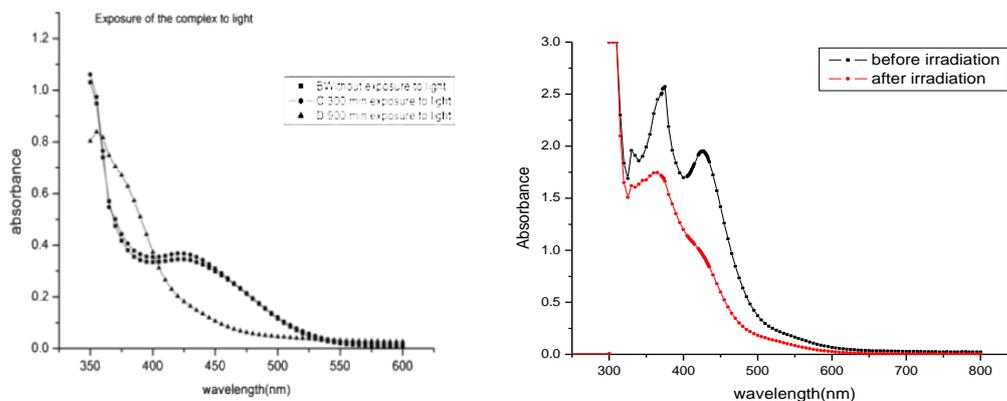


Fig.1.a. Direct photolysis of [Pd(phen)(tsa)] **Fig1.b.** Direct photolysis of [Pd(tsa)₂], before For 300 and 900 minutes of irradiation and after irradiation(30 min)

The loss in absorbance after exposure to sunlight suggest the chemical reaction between complex and oxygen in presence of light i.e. photo-oxidation.

3.4 :Self-sensitized photo-oxidation:

Photosensitization is the transfer of energy from a photochemically excited molecule to an acceptor, often oxygen, to form reactive singlet oxygen (¹O₂). The complexes under investigation show decay as a function of irradiation time in absence of sensitizer. Air saturated solution of [Pd(phen)(tsa)] in DMF (4 x 10⁻⁴ M) was irradiated. The course of photolysis was monitored by recording the absorption spectra in the visible region as a function of irradiation times (Fig.2.a) The initial increase followed by decrease in absorbance at 430 nm is accounted for the decay of [Pd(phen)(tsa)] as a result of photolysis. The band at 430 nm disappears after long irradiation (8-9 h) (Fig.1a)

Air saturated solution of [Pd(tsa)₂] in DMF(4 x10⁻⁴ M) was irradiated .The course of photolysis was monitored by recording the absorption spectra in the visible region as a function of irradiation time (Fig.2(b))The decrease in absorbance at 440 nm is accounted for the decay of [Pd(tsa)₂] as a result of photolysis. The band at 440 nm disappears after irradiation (2-3 h) to convert all the complex into new product(s).(Fig.1.b).

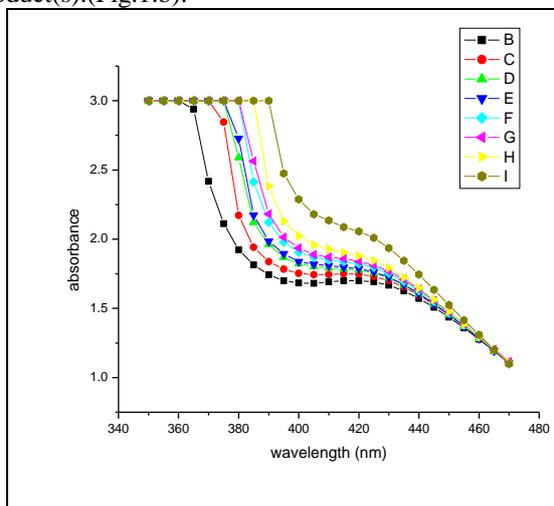


Fig.2.a. Absorption spectra as a function of irradiation time for [Pd(phen)(tsa)]

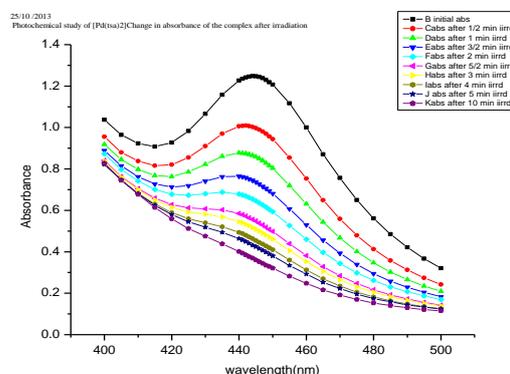


Fig.2.b. Absorption spectra as a function of irradiation time for [Pd(tsa)₂]

The Molecular oxygen saturated solution of [Pd(phen)(tsa)] and [Pd(tsa)₂] in DMF were quite stable in the dark. No change in absorbance is observed in nitrogen saturated solution of [Pd(phen)(tsa)] in DMF after irradiation. However more than 90% of the photo-oxidation of this complex (0.2 mM) is quenched when irradiated in presence of NaN₃ (0.4 mM).This confirms the involvement of singlet oxygen[10]. However the nitrogen saturated solution of [Pd(tsa)₂] in DMF show a different behavior, the peak at 440 nm disappears in presence of nitrogen with increased rate of photolysis. Similar observations were recorded in the presence of NaN₃ in the reaction mixture.(fig.3)

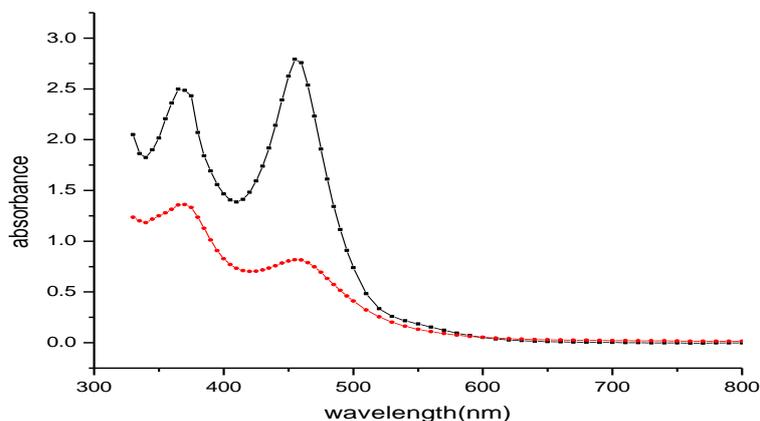


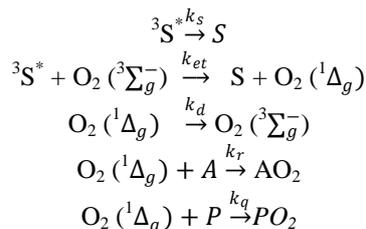
Fig.3 [Pd(tsa)₂] (0.4mM) in presence of NaN₃ (2mM) -●- complex , -●- complex+NaN₃

This may be due to formation of Pd-azido complex which is reported to undergo photo- reduction of the metal[20] .

3.5:Determination Rate constant of the reaction between singlet oxygen and complex

To study kinetics of the photochemical reaction, sensitized photo-oxygenation of a substrate /complex (A) in the presence of second substrate (P) which also reacts with singlet oxygen is considered[21]. The sequence of photochemical events leading to the formation of ¹O₂ and the channels of subsequent decay is summarized as:





Where *S* represents photosensitizer, ¹*S* represents its singlet excited state, ³*S* is its first triplet state. *k_d* is rate constant of quenching of ¹O₂ by solvent-DMF. *k_r* is the rate constant of chemical quenching of ¹O₂ by the substrate. *k_q* is the rate constant for chemical quenching by the probe [21,23].

The rate constant of reaction between singlet oxygen and substrate (A) were determined in solution containing a photosensitizer(PS) and a probe molecule (P) and carrying the experiment as substrate concentration. Experiment were carried out using various complex concentrations (0.215 mM) with DPBF(77.6 μM) and anthracene (0.1 μM) as sensitizer in DMF as solvent. The progress of the reaction before and after irradiation at various time intervals was monitored by measuring the absorbance. The slopes (S) of the plots of bleached absorbance (-ΔA) vs irradiation time for five different substrate(0.1-0.5 mM) concentrations are compared with the slope (S₀) of the same plot in the absence of substrate¹². Fig.5.a and b shows a plot of [S₀/S] against 1 / [complex] yields a straight line plot with a gradient of (k_d + k_q[P] / k_r). The values of rate constant (k_r) determined for [Pd(phen)(tsa)] and [Pd(tsa)₂] and using [Pd(tsa)₂] as probe, the rate constant for DPBF in DMF determined by above method are as shown in table 1

Table1: Quenching rate constant (k_r)

Quencher	probe	solvent	Rate constant (k _r) M ⁻¹ s ⁻¹
[Pd(phen)(tsa)]	DPBF	DMF	1.56 × 10 ⁹
[Pd(tsa) ₂]	DPBF	DMF	1.40 × 10 ⁹
DPBF	[Pd(tsa) ₂]	DMF	9.25 × 10 ¹⁰

The rate constant determined using DPBF as probe and DMF as solvent suggests that both complexes are as quenchers of singlet oxygen. k_r for DPBF is ~ 100 times more than that of complexes.

Quantum yields for formation of singlet oxygen:

Photosensitization is the most frequently used method for producing singlet oxygen. To measure the number of molecules of singlet oxygen produced as a function of number of photons absorbed in terms of absolute complex, a comparative actinometry has been carried out where a standard photosensitizer (of known φ_Δ) was irradiated under same conditions and the samples were optically matched. The quantum yield for singlet oxygen formation for the compound of interest can be calculated from the equation [22-23]

$$\phi_{\Delta}(U) = \phi_{\Delta}(St) \times \frac{S(U)}{S(St)}$$

where U is unknown sensitizer and St is standard sensitizer . S is the slope of the bleaching of the probe absorbance with irradiation time(fig.4)

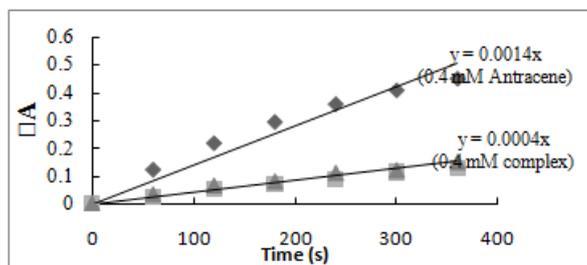


Fig.4 Bleaching of probe absorbance(ΔA) with irradiation time(second)

The φ_Δ for [Pd(phen)(tsa)] (0.4mM) and [Pd(tsa)₂] (0.4mM) has been determined using anthracene (0.1μM) as sensitizer and DPBF (3.1μM) as probe and DMF as solvent is found to be 0.2 for both the complexes. The values for quantum yield and quenching rate constant further confirm self-sensitized photo-oxygenation of Pd(II) complexes.

Effect of mixed solvent:

Air saturated solution of the [Pd(phen)(tsa)] (0.4 mM) and [Pd(tsa)₂] (0.4mM) in 10 % water –DMF was irradiated with light of wavelength 300-800 nm for different time intervals. The decrease in absorbance was measured on spectrophotometer. The rate of photo-oxidation was compared with that in pure DMF. (Fig.5.a,b). There is 40-50 % decrease in rate in 10% water-DMF as compared to pure DMF

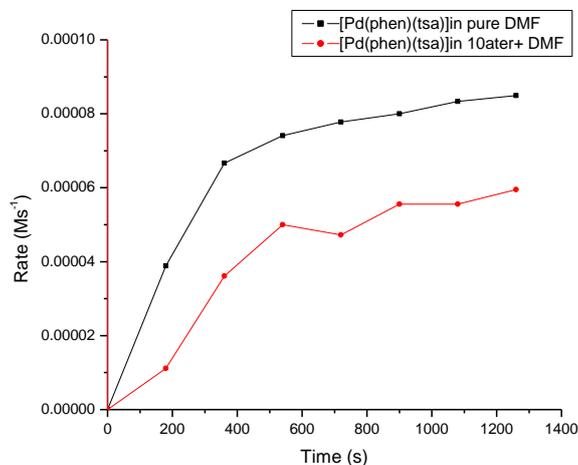


Fig 5a Effect of mixed solvent on Rate of photo-oxidation of [Pd(phen)(tsa)]

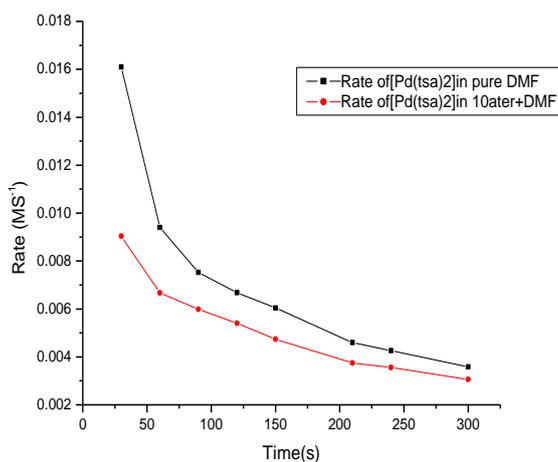


Fig 5 b. Effect of mixed solvent on Rate of photo-oxidation of [Pd(tsa)₂]

The quenching of this reaction in presence of water may be explained by the fact that the life time of ¹O₂ in water is very short (2μsec).So in aqueous medium only the most reactive compounds towards ¹O₂ attack could compete with such fast thermal quenching[24,25]. In DMF,the lifetime of ¹O₂is greater than in water,therefore the rate of photo-oxidation is faster in 100%DMF than in 10% water-DMF mixture.

IV. Conclusion

Identical photochemical behavior of the complexes under study confirms that DMSO can be replaced by water for the present synthesis. The change in absorbance of the complex before and after irradiation shows that the quenching is via chemical reaction between complex and singlet oxygen i.e. [Pd(phen)(tsa)] and [Pd(tsa)₂] undergo self-sensitized photo-oxidation with ¹O₂ as an intermediate. The values of rate constant suggest that these complexes are good quenchers of singlet oxygen.Rate of photo-oxidation decreases in presence of aqueous DMF as solvent. In addition to the biological activity,thesePalladium complexes are useful as photocatalyst in photooxidation reaction.

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