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Chemiluminescent studies of t-butylhydroperoxide with phenyl hydrazine hydrochloride in the presence and absence of luminol

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ABSTRACT

The chemiluminescence (CL) accompanying the oxidation of phenyl hydrazine with t-butylhydroperoxide in alkaline medium was studied in the presence and absence of luminol. The reaction occurring between phenyl hydrazine and alkaline (KOH) solution of aqueous t-butylhydroperoxide leads to the production of nitrogen gas with simultaneous emission of light (CL), which has been detected by PMT and recorded with the aid of PC using interface. The CL intensity was enhanced by addition of 10^{-3} M luminol solution. The influence of concentration of various constituent of reaction was investigation. The effect of antibiotic sensitizer aureomycine has also been studied.

Key words: Chemiluminescence, Phenyl hydrazine hydrochloride, Luminol, t-butylhydroperoxide (t-BuOOH), Aureomycine.

INTRODUCTION

Chemiluminescence (CL) is the simultaneous production of electromagnetic radiation (UV, Visible or IR) observed when a chemical reaction yields an electronically excited intermediate or product, which either luminesces or donates its energy to another molecule which then luminesces[1].

Hydrazine and its derivatives are often used as high energy propellant in space shuttle program and it is an important precursor in polymer industry, pesticides and pharmaceuticals[2]. Tsaplev's proposal for an excited molecular nitrogen from the oxidation of linear hydrazide stemmed from his work on the reaction of hydrazine with hypochlorite[3-4], Tsaplev suggested that excited dinitrogen produced further reacts to form an intermediate and a nitrogen monoxide emitter. Energy transfer to sensitizers and quenchers was thought to occur from the excited nitrogen intermediate. Safavi and Baezzat examined the oxidation of hydrazine with N-bromosuccinamide in presence of di flourescein and suggested that this efficient fluorophore accepted energy from an excited state of molecular nitrogen [5].Shakhashiri and Willium pointed that reaction between hypohalites is also chemiluminescent[6]. Cheknov and co-worker found that addition of hypochlorite to a t-butylhydroperoxide solution is accompanied by chemiluminescence burst whose intensity increases with increasing hypochlorite concentration as well as increasing t-butylhydroperoxide concentration[7]. In several known chemiluminescent reactions organic sensitizer participate as energy acceptors and effective emitters[8-10]. Therefore it has been thought to explore the reaction of phenyl hydrazine salt with t-butylhydroperoxide in presence and

absence of luminol and aureomycine (chlortetracycline).

EXPERIMENTAL

The reagents used for present investigation were phenyl hydrazinehydrocloride, KOH, t-BuOOH, aureomycine and luminol. The entire chemicals used in present investigation were taken in solution form and the solutions were prepared by using AR grade material in doubly distilled water. The alkaline and aqueous solution of t-butyl hydro peroxide was prepared by using $5x10^{-1}$ M KOH solution. Solution of different strength were prepared and tested. The strength at which the most intense CL was obtained was selected for further investigation.

Assembly for CL measurements essentially consisted of a chemiluminescence cell, high voltage power supply, light detector, digital multimeter and a PC linked through interface. The kinetics of chemiluminescence was recorded with a RCA 931A photomultiplier tube (PMT), the PMT was directly fed to digital multimeter (scientific SM 5015) interfaced with PC. The chemiluminescence cell and PMT were placed in a light tight box. Two circular holes were made on the top surface of the box. One for placing syringe to inject aqueous sodium peroxide in the reactor and other for placing thermocouple in the CL cell, the reactor were highly transparent glass tube 1 cm diameter and 5 cm length made of IMX machine (USA), and kept in just below the circular hole in which syringe was placed, and in front of entrance window of photo receiving device.

RESULTS AND DISCUSSION

Chemiluminescence is produced when alkaline aqueous solution of t-butylhydroperoxide (t-BuOOH) is added to the aqueous solution of phenyl hydrazine hydrochloride.

Effect of Concentration of phenylhydrazine hydrochloride

The dependence of CL intensity when aqueous alkaline solution of t-butylhydroperoxide was added to the solution of different concentration of phenyl hydrazine hydrochloride is shown in fig. 1(a). It is seen that CL intensity increases with time attains a maximum value then decreases with time. It is also observed that CL intensity initially increases with increasing concentration of phenylhydrazine hydrochloride solution attains an optimum value for 10^{-1}M solution of then decrease with further increase in concentration of phenylhydrazine hydrochloride. The CL intensity of

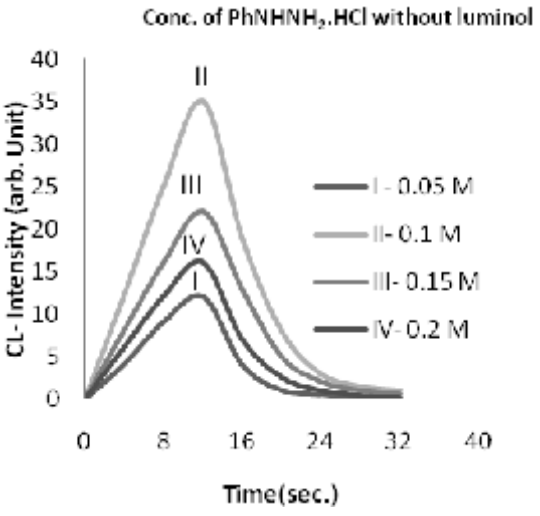


Fig.1(a): Time dependence of CL intensity for diff. con. of $PhNHNH_2$.HCl with luminol +KOH +t-BuOOH

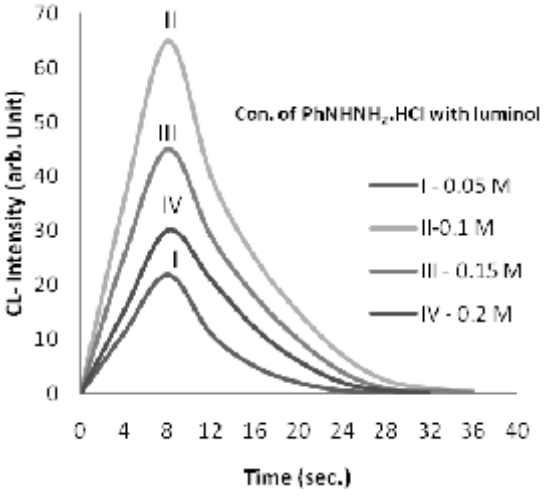


Fig. 1(b): Time dependence of CL intensity for differ. Con. of $PhNHNH_2$.HCl without luminol+KOH +t-BuOOH

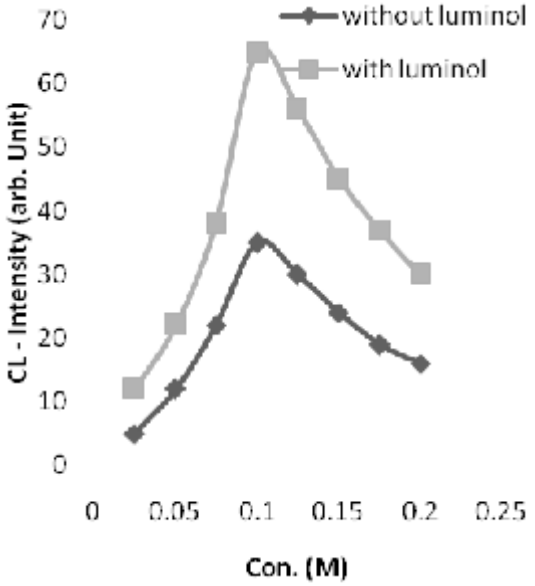


Fig. 1(c): Dependence of peak CL intensity on differs. the diff. vol of t-BuOOH with & without luminol +KOH+$PhNHNH_2$.HCl + KOH +t-BuOOH

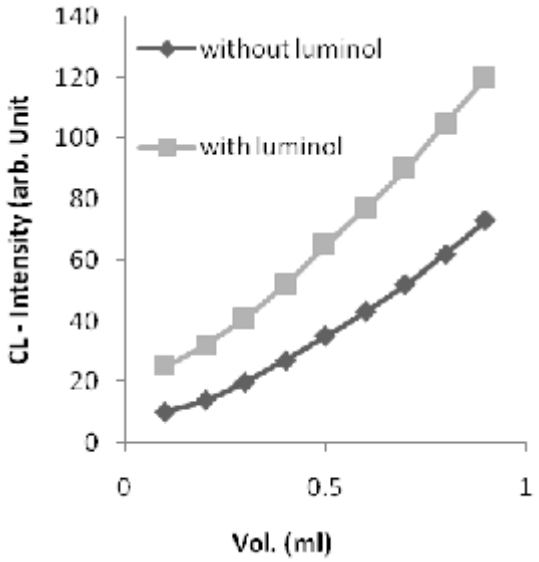


Fig.1 (d): Dependence of peak CL intensity of Con. of $PhNHNH_2$.HCl with & without luminol

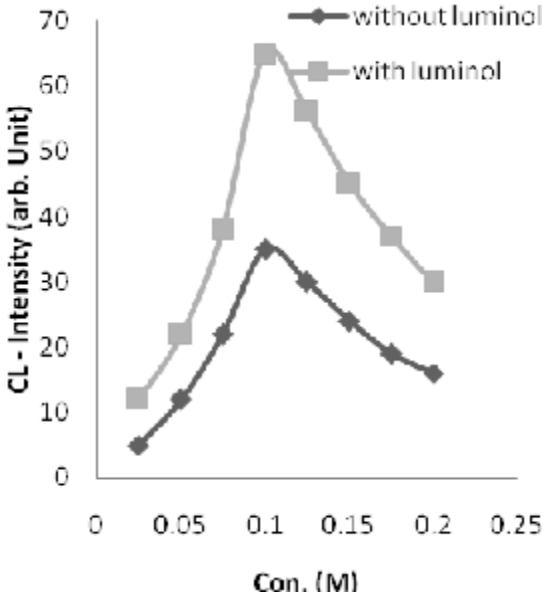


Fig. 1(c): Dependence of peak CL intensity on differs of $PhNHNH_2$.HCl with & without luminol

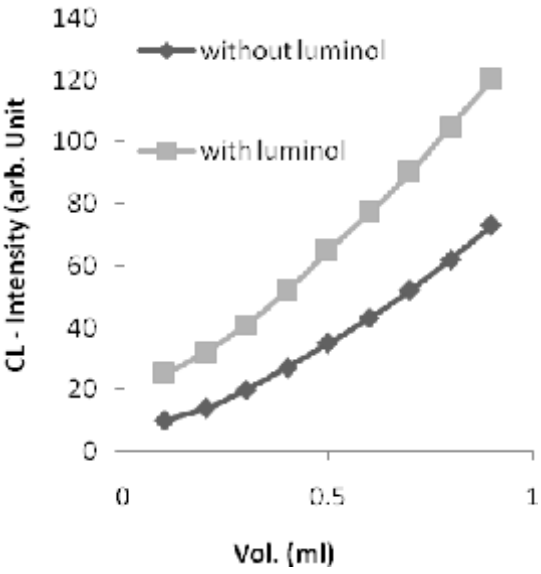


Fig. 1(d): Dependence of peak CL intensity of the diff. vol Con. of t-BuOOH with & without luminol +KOH+$PhNHNH_2$.HCl + KOH +t-BuOOH

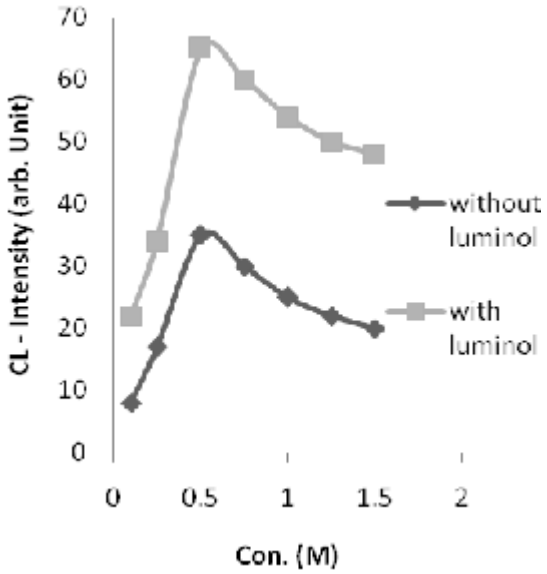


Fig. (e): Dependence of peak CL intensity on diff. for the Con. of KOH with & without luminol + t-BuOOH(10^{-4}M aureomycine) +KOH + t-BuOOH

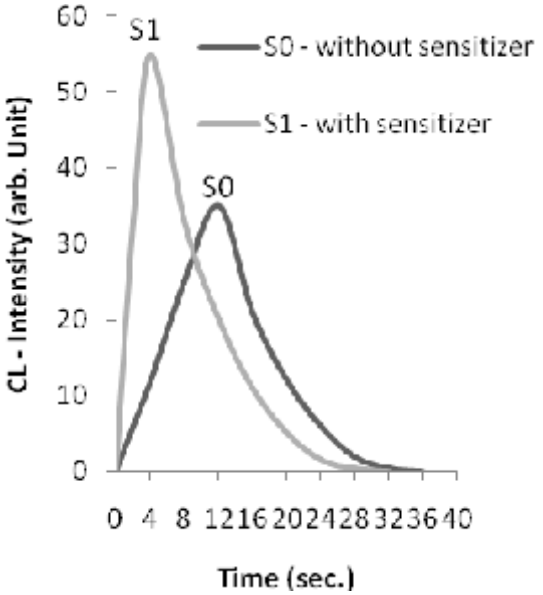


Fig.1 (f): Time dependence of peak CL intensity $PhNHNH_2$.HCl with & without sensitizer + $PhNHNH_2$.HCl

phenylhydrazinehydrochloride and aqueous alkaline t-BuOOH solution was found to be low (35 a.u.) but its intensity increases by a factor of 1.9(approx.) when 2×10^{-1} ml of 10^{-3}M luminol was added to the reaction mixture in the presence of luminol as shown in fig. (b). The same observation were obtained expect that the CL intensities obtained were higher than the observed value of reaction set without luminol. Dependence of peak CL intensity on different concentration of $PhNHNH_2$.HCl with and without luminol + 10^{-1}M t-BuOOH+$5x10^{-1}$M KOH is shown in fig. 1(c) separately.

Effect of Volume of t-BuOOH

For the reaction set containing 10^{-1}M $PhNHNH_2$. HCl and $5x10^{-1}$M aqe. KOH the volume of both reactants were fixed and the volume of aq. t-BuOOH was varied and CL intensity was recorded as shown in fig. 1(d). The same reaction was carried out in the presence of luminol (10^{-3}M). It was observed that as the volume of aqueous t-BuOOH increases the CL intensity increases almost linearly. Due to limitation of the experimental setup the volume of t-BuOOH can not be increased further beyond $5x10^{-1}$ ml. The same observations were obtained in presence of luminol but with increased CL intensities.

Effect of concentration of KOH

The effect of concentration of KOH on CL intensities was also studied by altering the concentration of KOH. It was found that CL intensity increases as concentration of KOH increases attains an optimum value (at $5x10^{-1}$M) then decreases. Similar observations were recorded in presence of luminol. The observations are shown in fig. 1(e).

Effect of Sensitizer

The influence of sensitizer on the luminescence intensity of phenylhydrazinehydrochloride and aq. t-BuOOH in alkaline medium was also studied by adding vary dilute solution of aureomycine (10^{-4}M) in absence of luminol. The observations are given in figure 1(f)

Mechanism

The observation obtained during the

reaction of phenyl hydrazine hydrochloride and aqueous t-butylhydroperoxide in presence of KOH and luminol can be explained on the basis of following plausible reactions.

$$PhNHNH_2.HCl + OH^- \rightarrow PhNHNH_2 + HCl + Cl^- \quad ...(1)$$

$$PhNHNH_2 + t\text{-}BuOOH \rightarrow [PhN{=}NH]^* + t\text{-}BuOH + H_2O \quad ...(2)$$

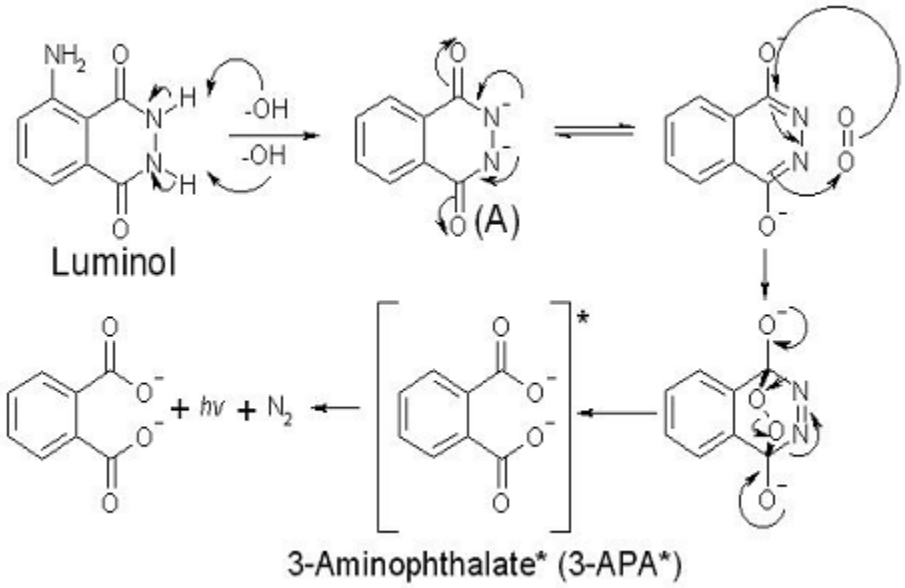
$$[PhN{=}NH]^* \rightarrow Ph\text{-}H + N_2^* \quad ...(3)$$

$$N_2^* \rightarrow N_2 + h\upsilon \quad ...(4)$$

In the presence of luminol.

$$KOH\,(aq.) \rightarrow K^+ + OH^- \quad ...(5)$$

Reaction (4) and (6) together enhances the luminescence.



CONCLUSION

The CL behavior of phenyl hydrazine hydrochloride with aqueous and alkaline t-BuOOH enhanced by luminol and sensitizer are reported. The proposed study undoubtedly could be applied for the detection of numerous analytes including the antibiotics whose concentration in different sample can be detected. It is hoped that this study will stimulate further investigations in this field.

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