CHEMILUMINESCENCE STUDIES OF CUMENE HYDROPEROXIDE WITH PHENYHDRAZINE HYDROCHLORIDE IN THE PRESENCE AND ABSENCE OF LUMINOL

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A B S T R A C T

The Chemiluminescence (CL) accompanying the oxidation of phenyl hydrazine with cumene hydroperoxide (CuOOH) in alkaline medium was studied in the presence and absence of luminol. The reaction occurring between phenyl hydrazine and alkaline (KOH) solution of aqueous cumene hydroperoxide (CuOOH) leads to the production of nitrogen gas with simultaneous emission of light (CL), which has been detected 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 sesitizer aureomycine has also been studied.

Keywords: Chemiluminescence, Phenyl hydrazine hydrochloride, Luminol, cumene hydroperoxide (CuOOH), Aureomycine.

1.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 hydrazine 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 fluorescein 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].Opeida and co-worker discussed Chemiluminescence during decomposition of cumene hydroperoxide in the presence of n-butyl pyridinium bromide[7].Cheknov and co-worker found that addition of hypochlorite to a t-butylhydroperoxide solution is accompanied by chemiluminescence brust whose intensity increases with increasing hypochlorite concentration as well as increasing t-butylhydroperoxide concentration[8].

In several known chemiluminescent reactions organic sensitizer participate as energy acceptors and effective emitters [9-11]. Therefore it has been thought to explore the reaction of phenyl hydrazine salt with cumene hydroperoxide in presence and ab sence of luminol and aurcomycine (chlorteracyline).

2. Experimental

The regents used for present investigation were phenyl hydrazine hydrochloride, KOH. CuOOH. Aureomycine and luminol. The entire chemicals used in present investigation were taken in solution from and the solutions were

prepared by using AR grade material in doubly distilled water. The alkaline and aqueous solution of cumene hydro peroxide was prepared by using $5x10^{-1}$ M KOH 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) interested 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 cumene hydroperoxide 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 enterance window of photo receiving device.

3.Result and Discussion

Chemiluminescence is produced when alkaline aqueous solution of cumene hydroperoxide (CuOOH) is added to the aqueous solution of phenyl hydrazine hydrochloride.

3.1Effect of Concentration of phenyl hydrazine hydrochloride:

The dependence of CL intensity when aqueous alkaline solution of cumene hydroperoxide was added to the solution of different concentration of phenyl hydrazine hydrochloride is shown in figure (1). 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 phenyl hydrazine hydrochloride solution attains an optimum value for 10^{-1}M solution of then decrease with further increase in concentration of phenyl hydrazine hydrochloride. The CL intensity of phenyl hydrazine hydrochloride and aqueous alkaline CuOOH solution was found to be low (35 a.u.) but its intensity increases by a factor of 1.9 (approx.) when $2x10^{-1}$ ml of 10^{-3}M luminol was added to the reaction mixture in the presence of luminol as shown in figure (2). 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 luminal + 10^{-1}M CuOOH + 5 X 10^{-1}M KOH is shown in figure (3) separately.

3.2 Effect of volume of CuOOH :

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 aqe. CuOOH was varied and CL intensity was recorded as shown in figure (4). The same reaction was carried out in the presence of luminol (10^{-3}M). It was observed that as the volume of aqueous CuOOH increases the CL intensity increases almost linearly. Due to limitation of the experimental setup the volume of CuOOH cannot be increased further beyond $5x10^{-1}$ ml. The same observations were obtained in presence of luminol but with increased CL intensities.

3.3 Effect of concentration of KOH:

The effect of concentration of KOH on 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 figure (5).

3.4 Effect of sensitizer:

The influence of sensitizer on the luminescence intensity of phenyl hydrazine hydrochloide and aq. CuOOH in alkaline medium was also studied by adding very dilute solution of auremycine (10^{-4}M) in absence of luminol. The observations are given in figure (6).

Mechanism:

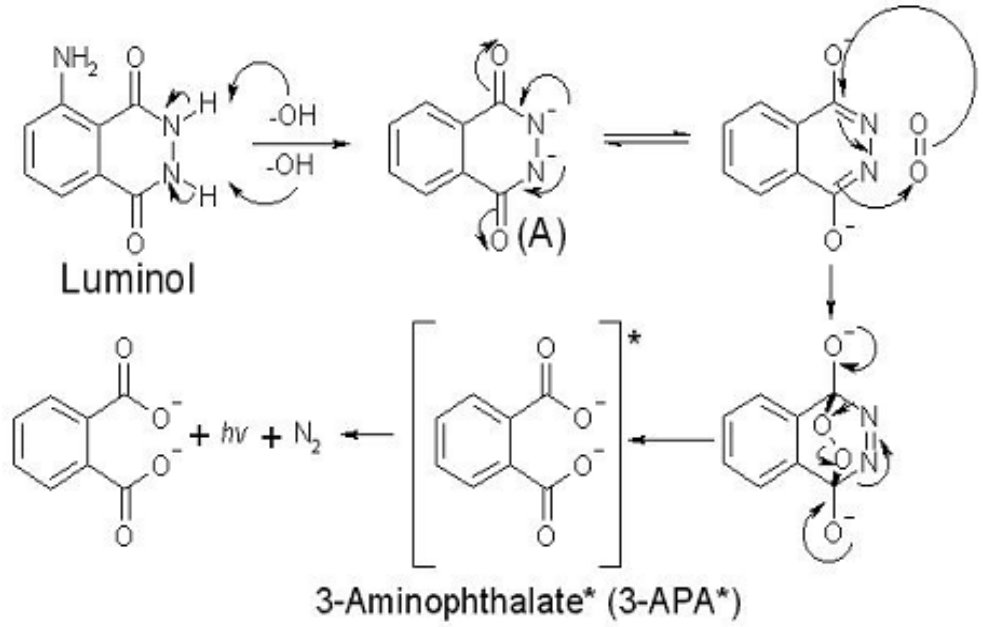
The observation obtained during the reaction of phenyl hydrazine hydrochloride and aqueous cumene hydroperoxide in presence of KOH and luminol can be explained on the basis of following plausible reactions.

$PhNHHN_2.HCl + OH \rightarrow PhNHNH_2 + HCl + Cl^-$ ……..(1)

$PhNHNH_2 + CuOOH \rightarrow [PhN=NH]^* + CuOOH + H_2O$ ……...(2)

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

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



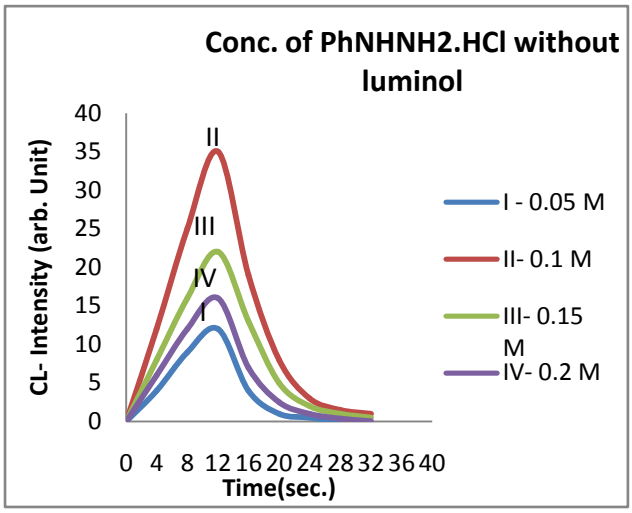


Fig.1.-Time dependence of CL intensity for differ Con. Of $PhNHNH_2.HCl$ without luminal + KOH + CuOOH

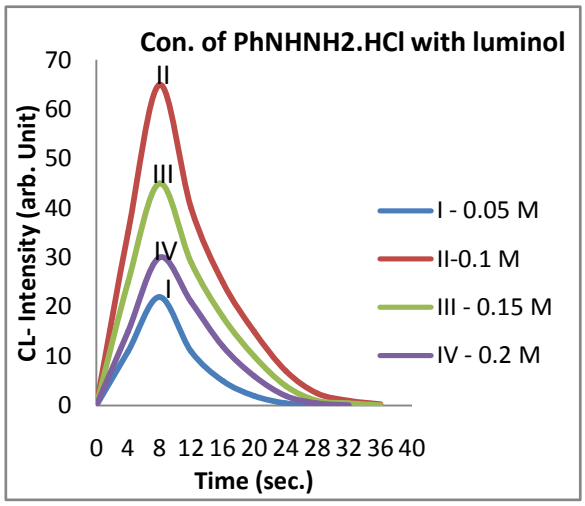


Fig.2.- Time dependence of CL intensity for differ Con. of $PhNHNH_2.HCl$ with luminol +KOH + + CuOOH

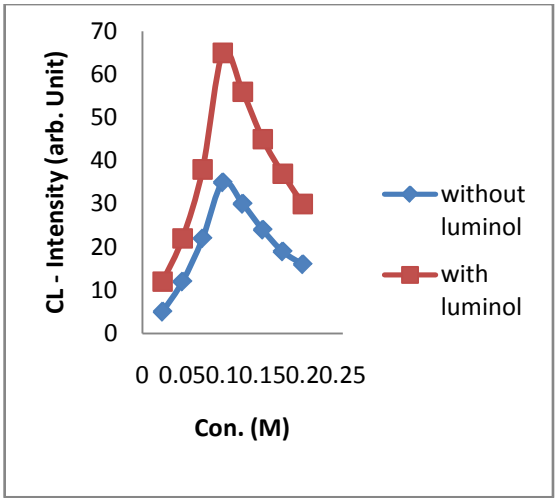


Fig.3- Dependence of peak CL intensity on diff. con. Of $PhNHNH_2.$ HCl with & without Luminol + KOH + CuOOH

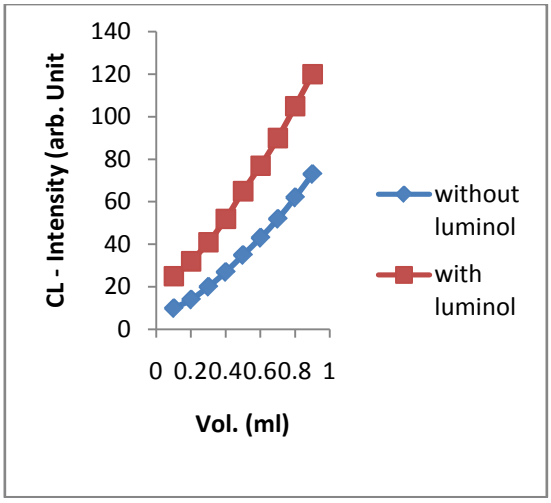


Fig.4- Dependence of peak CL intensity of the differ. vol. of CuOOH with & without luminol + KOH + $PhNHNH_2.HCl$

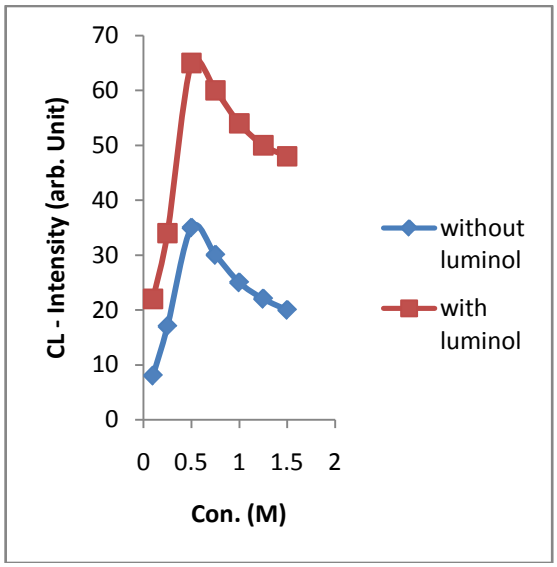


Fig.5.- Dependence of peak CL intensity on diff. the Con. of KOH with & without luminol + CuOOH + $PhNHNH_2$.HCl.

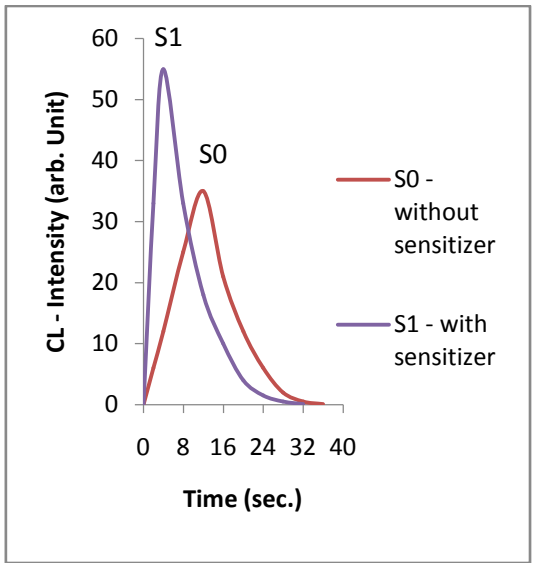


Fig.6.- Time dependence of peak CL intensity for $PhNHNH_2$.HCl with & without sensitzer (10^{-4} M auremycine) + KOH + CuOOH

4. Conclusion

The CL behavior of phenyl hydrazine hydrochloride with aqueous and alkaline CuOOH 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 study will stimulate further investigation in this field.

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References:

[1] Roda. A., Pasini R., Gurdigali M., Baraldini M., Muiani M., Mirasoli M.(2000).Fresenius.*J. Anal Chem.*, 366, 752.

[2] Schrnidt E.W.(1984).*Hydrazine and its derivative, preparation, properties & applications*, Wiley, New York.

[3] Tsaplev Yu. B.(1999). Russi,*J. Phy. Chem.*,73:1495.

[4] Tsaplev Yu. B. (1999). Russ. *J. Phy. Chem.*,73:1499.

[5] Safavi A., Baezzat M. R. (1998). *Anal. Chim. Acta*., 358:121.

[6] Shakhashiri B. Z., Williams L. G.(1976). *J. Chem. Edu.*, 53:358.

[7] Opeda I.A., Zalevskaya N.M., Gapsha N.M., Kachurin I.O.(2003). Inst. Fiz-Org. Khim. I Uglekhim., NAN Ukrainy. Donetsk, Ukraine. Neftekhimiya, 43:137.

[8] Chekanov A. V., Paneisenko O. M., Osipov A. N., Arnold J., Kazarinov K. D., Valdimiorov, IuA., Sergienko V. I.(2002). Biofizika,47:787.

[9] Wirat I. T., Ruengsitagoon ThongpoonC., Saisunee L.(2005). *Anal. Chem.Acta*, 541:103.

[10] Hen S., Liu E., Li H.(2006). *J. Biolumi. Chemlumi.*, 21: 106.

[11] Wang L. (2006).*Chem. Anal.* (Warsaw), 51:211.