Int. J. Chem. Sci.: 7(4), 2009, 2495-2500

CHEMILUMINESCENCE FORM ACETONITRILE WITH Na_2O_2 IN PRESENCE AND ABSENCE OF LUMINOL

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ABSTRACT

The chemiluminescence (CL) that accompanies the oxidation of acetonitrile with aqueous sodium peroxide in alkaline medium was studied in the presence and absence of luminol. The reaction occurring between acetonitrile and alkaline KOH solution of aqueous sodium peroxide lead to the production of oxygen gas with simultaneous emission of light (CL), which has been detected by PMT and recorded with the aid of PC using interface. The weak CL intensity was enhanced by addition of 10^{-3} M luminol solution. The influence of concentration of various constituents of the reaction and pH of medium was investigated. The effect of antibiotic sensitizer ciprofloxacin has also been studied.

Key words: Chemiluminescence, Acetonitrile, Luminol, Sodium peroxide, Ciprofloxacin.

INTRODUCTION

Acetonitrile is a volatile, colorless liquid with sweet ether like odour. It is a highly polar solvent used to extract fatty acids and animal and vegetable oil. Lu et al.[1] reported a new chemiluminescent reaction between basic aqueous H_2O_2 and acetonitrile[1]. The work done finds it application in immunoassay, DNA hybridization, and environmental monitoring and post chromatographic detection. Lau et al.[2] found that a non enzymatic CL reaction between luminol or flouresceine and oxygen species generating KCN as catalyst were rather fast and unsuitable for CL imaging. However, the speed of the reaction could be reduced by changing KCN catalyst for acetonitrile.

Chemiluminescence reaction between H_2O_2 and acetonitrile were found to be ultra weak[3, 4] and, hence to enhance its CL intensity, luminol can be used, which is the best

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known chemiluminescent compound. The luminol reaction has been used for the determination of oxidizing agents such as Cu^{2+} or Co^{3+}, which catalyses the chemiluminescence[5]. Luminol has been extensively used in medico-legal investigations[6]. The light producing pathway for the oxidation of luminol is complex and dependent on the reactive species that are present in the solution. According to the suggested mechanism, the diazoquinone intermediate is formed, which then reacts with hydrogen peroxide anion to form an amino phthalate emitter. The luminescence from the oxidation of luminol with hypohalites is therefore, greatly enhanced due to addition of hydrogen peroxide[7, 8].

Here, we present study of chemiluminescence reaction occurring between acetonitrile and aqueous alkaline sodium peroxide in presence and absence of luminol and antibiotics like ciprofloxacin and suggest a mechanism for enhancement of luminescence due to luminol and the antibiotics.

EXPERIMENTAL

The reagents used for present investigation were acetonitrile, KOH, Na_2O_2, ciprofloxacin 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 sodium peroxide was prepared by using 0.5 M KOH solution. Solution of different strengths 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 the other for placing thermocouple in the CL cell. The reactors were highly transparent glass tube, 1 cm diameter and 5 cm length, made IMX machine (USA), and kept it just below the circular hole in which syringe is placed, and in front of entrance window of photo receiving device.

RESULTS AND DISCUSSION

Chemiluminescence is produced, when alkaline aqueous solution of sodium peroxide is added to the solution of acetonitrile.

Effect of concentration

The dependence of CL intensity, when aqueous alkaline solution of sodium peroxide was added to the solution of different strength of acetonitrile is shown in Fig. 1(a). It is seen that CL intensity increases with time and attains a maximum value; then decreases with time. It is also observed that CL intensity initially increases with increasing strength of acetonitrile solution and attains an optimum value for solution of strength 30%; then decreases with further increase in strength of acetonitrile. The CL intensity of acetonitrile and aqueous alkaline 0.1M Na_2O_2 solution was found to be low (25 a.u.) but its intensity increases by a factor of 1.6 (approx.), when 0.2 mL of 10^{-3}M luminol was added to the reaction mixture in the presence of luminol as shown in Fig. 1 (b). The same observations were obtained except that the CL intensities obtained were higher than the observed value of reaction set without luminol. Dependence of peak CL intensity on different concentrations of acetonitrile with and without luminal + Na_2O_2 + KOH is shown in Fig. 1(c), separately.

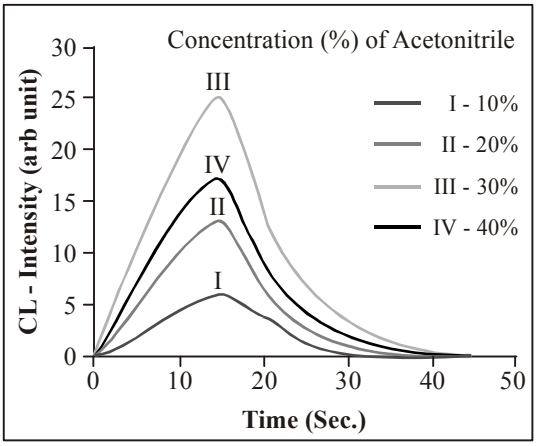


Fig. 1(a): Time dependence of CL intensity for different concentration of aceonitrile without luminol + KOH + Na_2O_2

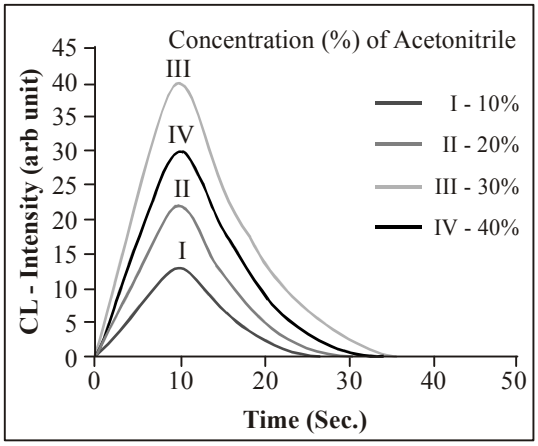


Fig. 1(b): Time dependence of CL intensity for different concentration of aceonitrile with luminol + KOH + Na_2O_2

Effect of volume of Na_2O_2

For the reaction set containing 30% acetonitrile and 0.5M aq. KOH the volume of both reactants were fixed and the volume of aq. 0.1M Na_2O_2 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 Na_2O_2 increases, the CL intensity increases almost linearly. Due to limitation of the experimental setup, the volume

of Na_2O_2 cannot be increased further beyond 0.5 mL. The same observations are obtained in presence of luminol but with increased CL intensities.

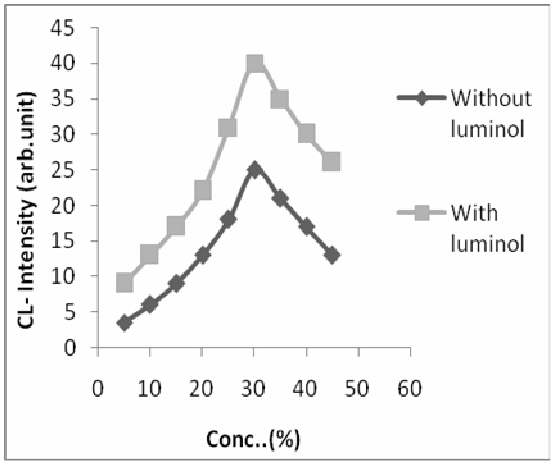


Fig. 1(c): Dependence of peak CL intensity on different concentration with and without luminol

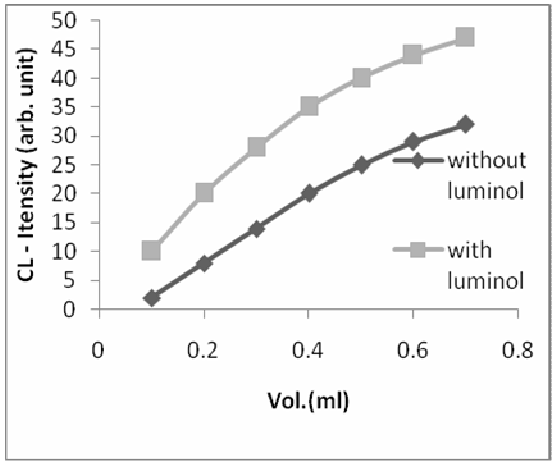


Fig. 1(d): Dependence of peak CL intensity on the vol. of 0.1 M Na_2O_2 with and without luminol

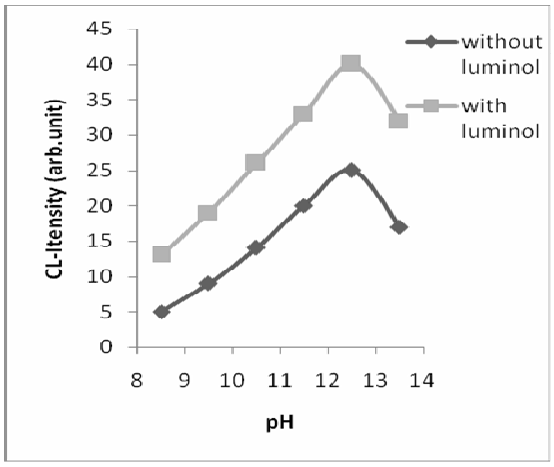


Fig. 1(e): Dependence of peak CL intensity on different pH of KOH + CH_3CN + Na_2O_2 + with and without luminol

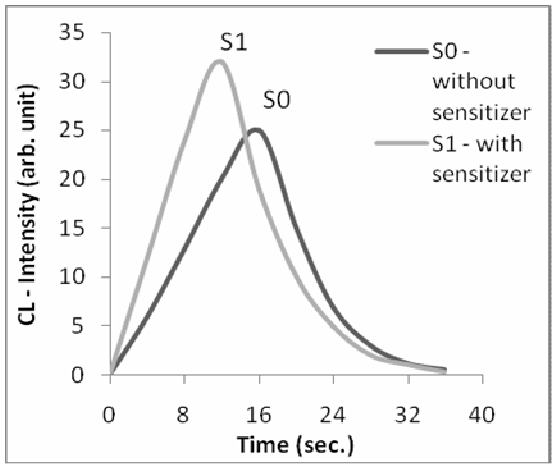


Fig. 1(f): Dependence of peak CL intensity for the acetonitrile + Na_2O_2 + KOH with and without sensitizer (10^{-4}M Ciprofloxacin)

Effect of pH

The effects of pH on CL intensities were also studied by altering the concentration of KOH (pH). It is observed that CL intensity increases as the pH increases and attains an optimum value (at 12.5 pH); then decreases. Similar observations were recorded in the presence of luminol. The observations are depicted in Fig. 1(e).

Effect of sensitizer

The influence of sensitizer on the luminescence intensity of acetonitrile and aq. Na_2O_2 in alkaline medium was also studied by adding vary dilute solution of ciprofloxacin (10^{-4}M) in absence of luminol. The observations are depicted in Fig. 1(f).

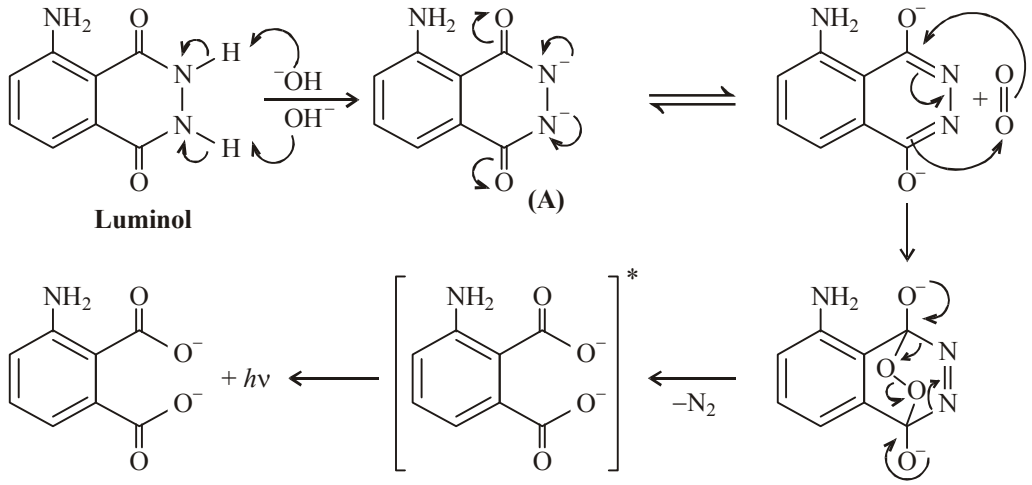
Mechanism

The observations obtained during the reaction of acetonitrile and aqueous sodium peroxide in presence of KOH and luminol can be explained on the basis of following plausible reactions

$$Na_2O_2 + 2\ H_2O \longrightarrow H_2O_2 + 2\ NaOH \quad \ldots.(1)$$

$$CH_3CN + H_2O_2 \longrightarrow CH_3\ CO\ NH_2 + {}^1O_2 + H_2O \quad \ldots.(2)$$

$${}^1O_2 + H_2O_2 \longrightarrow 2\ OH + O_2 \quad \ldots.(3)$$



….(4)

CONCLUSION

The CL behavior of acetonitrile with aqueous and alkaline Na_2O_2 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 samples can be detected. It is hoped that this study will stimulate further investigation in this field.

ACKNOWLEDGEMENTS

The author are thankful to Dr. (Smt) A. Kaushik , Principal and Dr. (Ku.) C. Das Prof. & Head, Dept. of Chemistry, Govt. ERR Sc. PG College Bilaspur (C.G.) for providing experimental facilities.

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Accepted: 03.08.2009