

STUDY OF CHEMILUMINESCENCE IN FERROUS SULPHATE AND FERROUS AMMONIUM SULPHATE

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ABSTRACT

The chemiluminescence behavior during redox reaction of ferrous sulphate and ferrous ammonium sulphate with hydrogen peroxide in alkaline medium is reported. The reactions were also tested for their chemiluminescence behavior in presence of activators like alkaline earth metal ions and common chemical acid base indicators like phenolphthalein. The study of experimental parameters affecting the redox process and detection was performed using standard chemiluminescence (CL) setup. The CL glow curve of reaction at different concentration has been recorded for better understanding of mechanism of redox process. A Plausible mechanism of the reaction based on CL behavior has been suggested.

Keywords: *Chemiluminescence, Ferrous Sulphate, Ferrous Ammonium Sulphate, Hydrogen Peroxide, Chemical Kinetics*

INTRODUCTION

Emission of energy in the form of visible light during chemical process is known as chemiluminescence (CL). The studies on CL properties of materials provide an insight of chemical reaction and related energy transport process, which normally cannot be understood by other methods. Light emission in chemical reaction requires following conditions (Adam and Clinto, 1982; Ugarova *et al.* 1998; Scholmerich *et al.* 1982; Devine *et al.* 1983).

1. The energy released should be higher than that of the electronically excited product or intermediate molecule.
2. Product must be fluorescent molecule so that the transformation of the excited molecule to the ground state is accompanied by visible light emission or the reaction mixture has to include acceptor molecules with fluorescent properties.

CL appears during oxidation reaction or free radicals recombination. To date most of the work on CL has been carried out on organic materials Ugarova *et al.* (1998). However, inspite of extensive research there are still many open questions concerning key stages at radical intensity are important factors for CL they have not been given due importance. It is to be noted that only limited studies have been made on CL of organic reactions (Campbell *et al.* 1994; Seliger and McElory 1964; Seliger, 1975; Bushnell, 1981).

This paper includes the studies of the CL of reaction of inorganic materials like ferrous sulphate & ferrous ammonium sulphate with hydrogen peroxide in acidic medium. It is speculated that the proposed study would provide a better understanding of kinetics of chemical reaction of peroxide with inorganic salt.

MATERIALS AND METHODS

Assembly for CL measurement essentially consists of a chemiluminescent cell, high voltage power supply, light detector, signal processor and X-Y recorder. Figure-I shows the block diagram of the system. The chemiluminescence cell and a photomultiplier tube (PMT) were place in a light tight box. A circular hole is made on the top surface of the box for placing syringe to inject the final solution in the

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cuvate. The cuvate is fitted inside the top surface of light tight box and it rest just below the circular hole. The cuvate is a highly transparent glass tube of 1.0cm diameter and 5cm length and made by IMX machine (USA). The box was covered with the black cloth and syringe is placed on the hole. The medico syringe of disproven co. with double cock is used to inject the final solution in the cuvate.

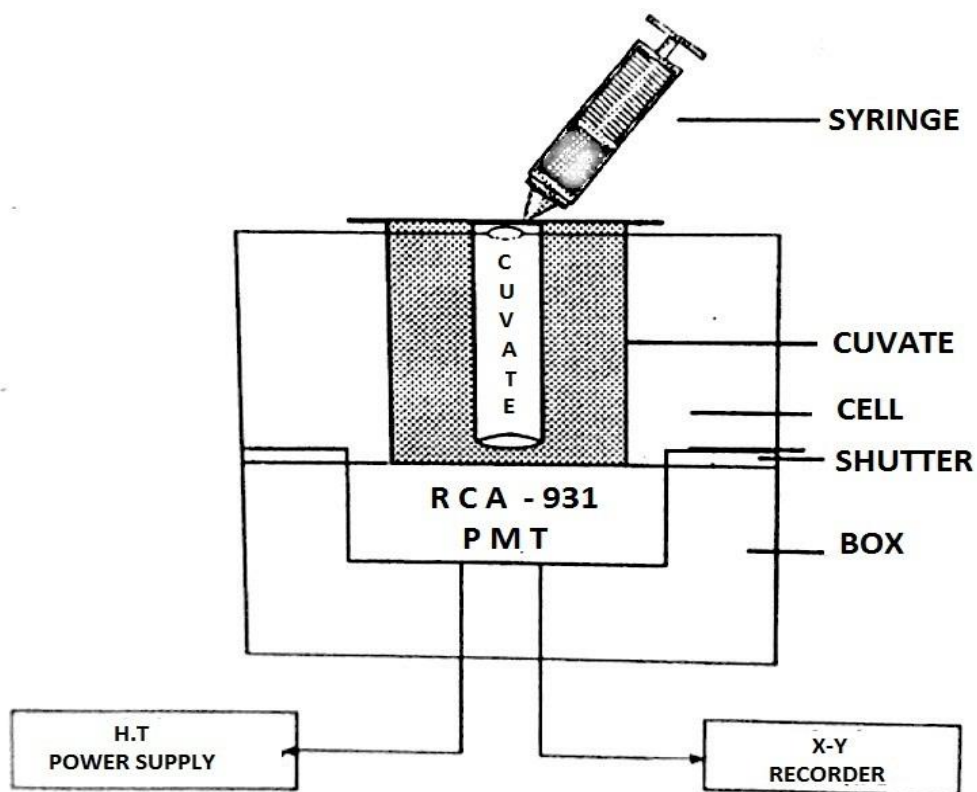


FIG 1 : EXPERIMENT SETUP OF CHEMILUMINESCENCE

The light emitted during the reaction was detected by RCA 931A photomultiplier tube. High voltage power supply was used to bias the various dynodes of the PMT. All the measurement was carried out in dark. For each measurement 0.5ml of hydrogen peroxide (20 volume qualigens co.) was added in the cuvate through syringe. All the chemicals were taken in solution form (0.5ml) and the solution were prepared by using AR grade material adopting standard method describing method described in the text book.

RESULTS

(a) The time dependence of CL intensity was observed when hydrogen peroxide was added to the aqueous solution of ferrous sulphate. It is evident that the CL intensity initially increases linearly with the time attains an optimum value than decreases with increasing time. It is observed that it increases with the use of sensitizer (phenolphthalein). Shown in Fig 2.

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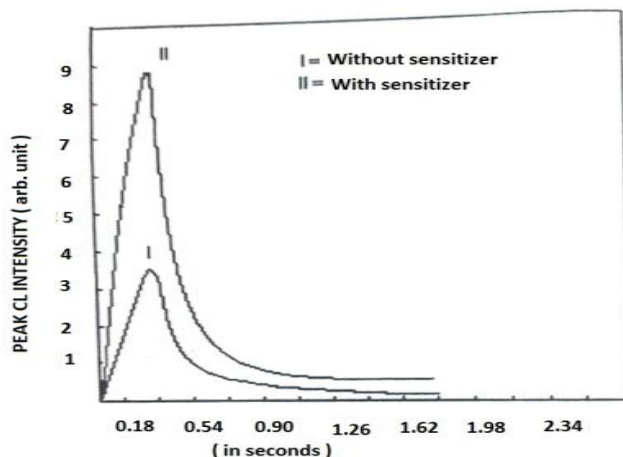


Fig 2 Time dependence of peak CL intensity of ferrous sulphate and H₂O₂

(b) The dependence of CL intensity on concentration of ferrous sulphate keeping concentration of H₂O₂ constant was observed. The CL intensity has been found to increase with increasing concentration attains a maximum value at 0.1N, then decreases with increasing concentration. However, we have also observed that in the presence of sensitizer (phenolphthalein) the optimum CL intensity is obtained at 0.05N, shown in Fig. 3.

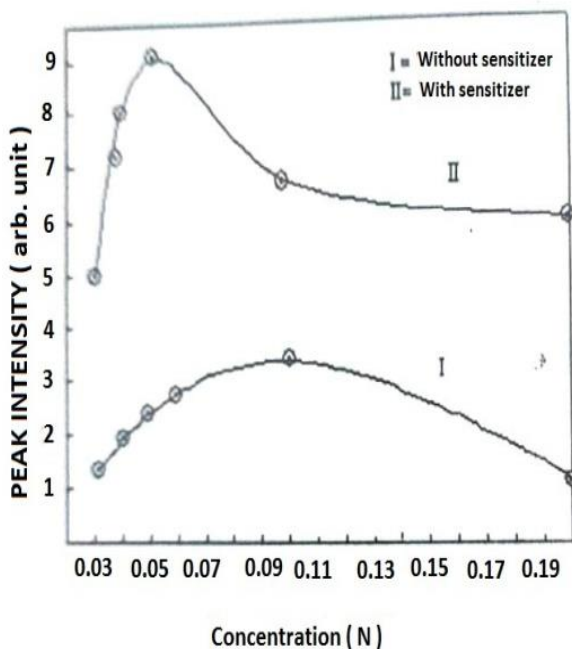


Fig. 3 Dependence of Peak CL intensity on different concentrations of FeSO₄ at fixed amount of H₂O₂

(c) When hydrogen peroxide was added to the aqueous solution of ferrous sulphate the CL peak lies at 482 nm and 585 nm. It is also observed that the CL spectra show a broad band centered around 482 nm when CL reaction takes place in presence of phenolphthalein. Shown in Fig 4.

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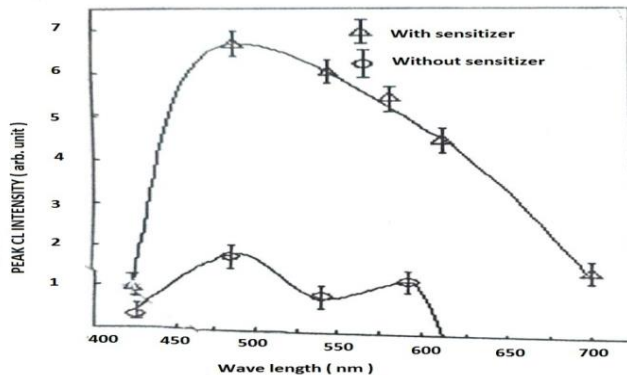


Fig. 4 Emission spectra of FeSO₄ and H₂O₂

(d) When hydrogen peroxide was added to the aqueous solution of ferrous ammonium sulphate the CL intensity initially increases linearly with time, attains an optimum value than decreases with increase in time. It is also observed that the CL intensity has been found to become doubled in the presence of sensitizer (phenolphthalein) Shown in Fig 5.

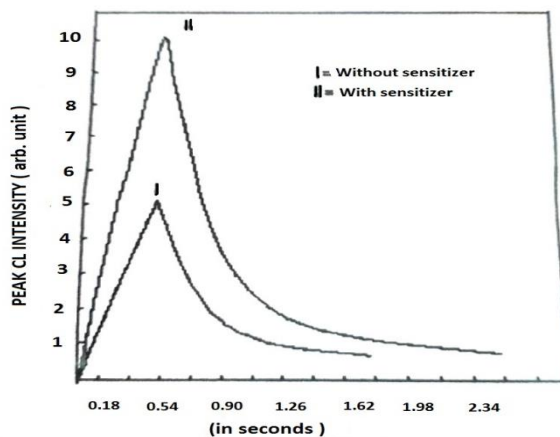


Fig.5 Time dependence of CL intensity of Ferrous ammonium sulphate

(e) The dependence of CL intensity with ferrous ammonium sulphate keeping concentration of H₂O₂ constant was observed. The CL intensity increases on increasing concentration but after an optimum value at 0.1N, it decreases with further increase in concentration. It was also observed that in presence of phenolphthalein the optimum is also at 0.1N with amplified intensity. Shown in Fig 6.

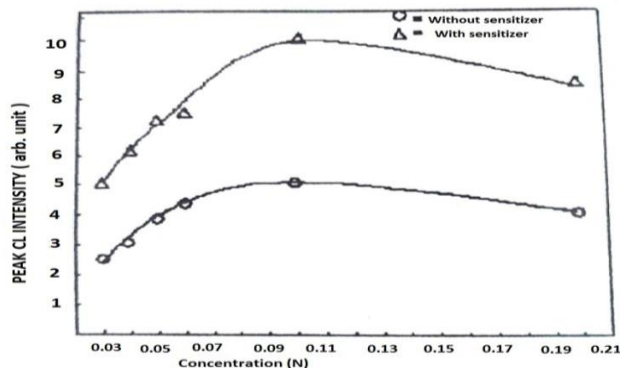


Fig.6 dependence of CL intensity on the concentration of ferrous ammonium sulphate

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(f) When hydrogen peroxide was added to ferrous ammonium sulphate, the CL emission peak in lies at 482nm. It was also observed that the peak in CL spectra lies at 482 nm in the presence of sensitizer (phenolphthalein) shown in Fig 7.

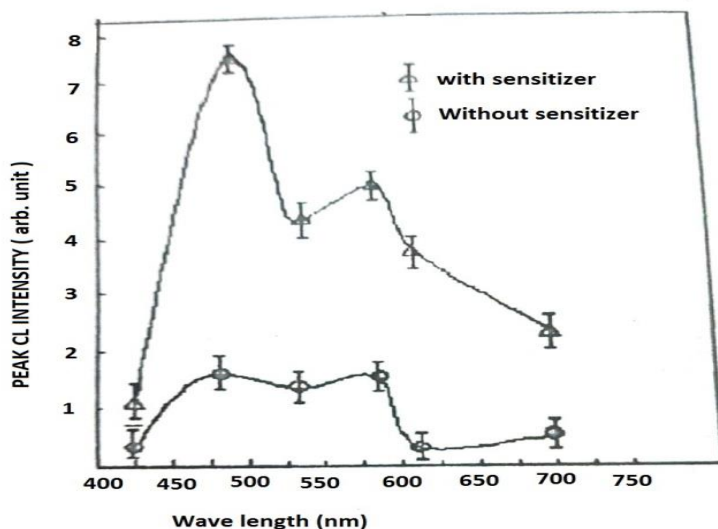
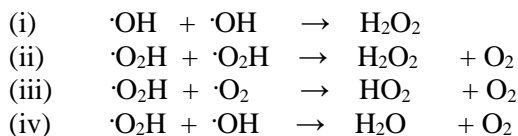


Fig.7 Emission Spectra of Ferrous Ammonium Sulphate

We have observed that the variation in amount of H₂O₂ does not show any considerable change in CL intensity but at very less amount CL intensity decreases. Further we have also found that the amount of phenolphthalein doesn't show any variation.

DISCUSSION

Present paper deals with the studies of CL reaction of potassium ferrous sulphate & ferrous ammonium sulphate with H₂O₂ in acidic medium. Both the salts ferrous sulphate and ferrous ammonium sulphate in aqueous solution exist largely as [Fe(H₂O)₆]²⁺. Many redox reactions of H₂O₂ in aqueous solution are accompanied by CL of mostly of very low intensity. Its origin might be sought in reaction of hydroxyl and perhydroxyl radical, which appears as intermediate. In the absence of inorganic excitable molecule following radical recombination are of importance:



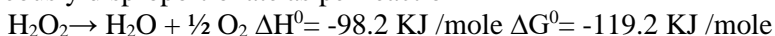
Reaction (i) do not lead to the excited state but in reaction (ii) (iv) oxygen in the excited state is believed to be produced. The transition state of oxygen emits light at 760nm or 1200nm. They are however not registered by the normal photomultiplier tube as light detector. Therefore, the observable CL of such reaction are believed to be closely associated with the known emission of O₂ dimers. Because of the weakness of CL of the reaction of H₂O₂ with better quantum yield, sufficient for spectroscopic investigation is surely non radical. In many reactions at with perhydroxyl radical are known as intermediate a weak blue green CL has been observed.

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In alkaline medium the addition of carbonate and bicarbonate to the solution of H₂O₂ under investigation produces increase in luminescence intensity with increase in carbonate concentration especially in the spectral region of 450nm to 550nm. In reaction of ferrous ion and H₂O₂ in the presence of KHCO₃ the CL intensity has been found to increase as compared to not using KHCO₃. The luminescence has been found to be much amplified by fluoresce like eosins.

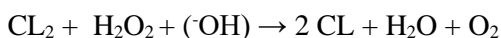
1. The varied and rich chemistry of H₂O₂ is due to (i) its ability to act as an oxidizing or as reducing agent in acidic or alkaline medium (ii) its ability to undergo proton acid base reaction to perform peroxonium salt. (iii) its ability to give peroxometal complexes with peroxy acid anion (Greenwood, Earnshaw, 1989).

The reduction potential data suggest that H₂O₂ is unstable w.r.t. water and oxygen and is spontaneously disproportionate as per reaction

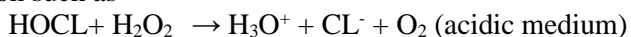


But in actual practice it decomposes negligibly and slowly. Metal surfaces, MnO₂ and traces of alkalis catalyze the decomposition.

2. It has been found that whenever acts as reducing agent oxygen is always evolved and sometimes it gives to a red chemiluminescence. Reaction of CL₂ with H₂O₂ in basic solution has been found to give red CL in O₂ bubbles due to O₂ in vibrationally excited state (Brown and Ogryzlo, 1964).



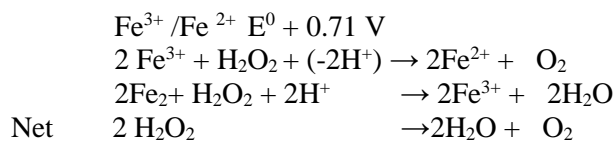
Reaction such as



has also been described in almost all texts.

The catalytic decomposition of aqueous solution of H₂O₂ can be viewed as a redox process and actually most homogeneous catalyst used for this reaction are redox couples of which oxidizing agent can oxidize (be reduced by H₂O₂ and reducing agent can reduce (be oxidized by) H₂O₂.

3. From thermodynamic data's it can be concluded that any complex with reduction potential between +0.695 and +1.776 VOLTS in acid solution should catalyze the reaction (Uri *et al.* 1962).



4. It is important to recognize that many reaction involving H₂O₂ and O₂ in solution are free radical ones (Uri *et al.* 1962).

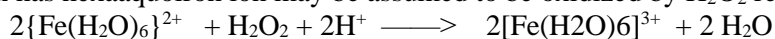
Oxidation of H₂O₂ in aqueous solution by CL₂, MnO₄⁻, Ce⁴⁺ etc and catalytic decomposition by Fe³⁺, I₂, MnO₂ etc has been studied in both cases by using label H₂O₂ having ¹⁸O which shows negligible exchange between H₂O₂ and H₂O all the O₂ formed when H₂O₂ is used as a reducing agent comes from H₂O₂ suggesting that oxidizing agent do not break O-O bond but simply removes electrons. However all the reaction are not hetrolytic and free radicals of OH and H₂O are sometimes involved. Free radicals in Fentons reagent Fe²⁺ / H₂O₂ have its own implication.

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5. During the reaction free radicals H₂O may be assumed to have caused the radicals combination thus producing CL through electronically excited state. In both the reaction the mechanism of chemically initiated electron exchange luminescence (CIEEL) takes place (McCapra *et al.* (1989).

CONCLUSION

The ferrous sulphate and the more stable double salt ferrous ammonium sulphate existing in aqueous solution has hexaquoiron ion may be assumed to be oxidized by H₂O₂ represented by the reaction-



In the acidic medium H₂O₂ may be assumed to give peroxonium ion which on reaction with ferrous produces hydroxyl radicals which in turn react with H₂O₂ producing superoxide ion similar to reaction of luminal and H₂O₂ in the presence of iron. During the reaction the radical recombination may result in chemiluminescence through electronically excited state since both ferrous sulphate and ferrous ammonium sulfate give same activator cation in solution. Hence the kinetics of the reaction with H₂O₂ for both the compounds are same.

The amplification of CL intensity in presence of common acid base indicator like phenolphthalein may be attributed to fluorescence character of phenolphthalein. The spectra observed at 482 nm may be attributed to the electronically excited complex formed between intermediate and substrate.

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