

Chemiluminescence Emission Reaction of Aldehyde with Hydrogen Peroxide and Luminol

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Abstract - Chemiluminescence of aldehydes (like formaldehyde, acetaldehyde, propionaldehyde and benzaldehyde) and hydrogen peroxide in presence and absence of luminol has been studied. Magnesium hydroxide was chosen for solution making alkaline. The peak CL intensity initially increases with concentration, attains an optimum value for a particular concentration then decreases with further increases in concentration of aldehydes. It is also observed that for all aldehydes maximum CL found for very low concentration (0.03M) of magnesium hydroxide. The CL intensity increases drastically in presence of 0.001M luminol and reaction becomes faster.

INTRODUCTION

An aldehyde is an organic compound containing a terminal carbonyl group. This functional group, which consists of a carbon atom bonded to a hydrogen atom and double bonded to an oxygen atom, is called the aldehyde group. The aldehyde group is also called the formyl or methanoyl group. Haruo et al. proposed that the bilirubin in an alkaline solution exhibits a weak CL under aerobic conditions. This spontaneous CL was markedly enhanced by the addition of various aldehydes¹. A continuous flow method for the determination of formaldehyde in urban air has been developed based on the CL reaction between hydrogen peroxide solution and gaseous formaldehyde in the presence of gallic acid in alkaline solution². Yang and Chang found that amoxicillin can react with potassium permanganate in an acidic medium to produce CL, which is greatly enhanced by formaldehyde³. Kamil et al. studied the formaldehyde in the denuder concentrate is on-line detected employing a chemiluminescence flow method based on a reaction of formaldehyde and gallic acid with hydrogen peroxide in an alkaline solution⁴. Kamil et al. again studied the different approaches were used at the optimization of CL determination of formaldehyde in water based on the reaction of formaldehyde, gallic acid and hydrogen peroxide in an alkaline solution⁵.

Survey of literature show that very limited investigations have been made on the CL of aldehydes and in most of the studies aldehydes were used as enhancer for CL of other compounds. No systematic investigation has been made on the CL of aldehydes with hydrogen peroxide. The present paper deals with the studies of the chemiluminescence reactions of aldehydes (like formaldehyde, acetaldehyde, propionaldehyde, benzaldehyde) with hydrogen peroxide in presence and absence of luminol.

EXPERIMENTAL

Assembly for CL measurements essentially consists of a chemiluminescence cell, high voltage power supply, light detector and a PC linked through interface. The chemiluminescence cell is a double walled cubical box and inner part of the cell is cylindrical. A heater coil is wound round the cylinder, which may be connected to a variac. A window was made on one sidewall of the CL cell in front of which the photomultiplier tube was placed to detect the light coming through the window, which is produced during the chemical reaction. The chemiluminescence cell and photomultiplier tube (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 solution in the cuvette and other for placing thermocouple in the CL cell. The cuvette is fitted inside the top surface of the light tight box and it rests just below the circular hole in which the syringe is placed. The cuvette was highly transparent glass tube of 1.0 cm diameter and 5 cm length made by IMX machine (USA). The box was covered with black cloth and syringe was placed on the hole. The light emitted during the reaction was detected by RCA 931A photomultiplier tube. The photomultiplier housing used for CL measurement. The housing is made of thick soft iron to provide a shielding from light. The slit arrangement at the window was provided for adjustment of the size of the window according to incident beam. For EHT input and the detector (PMT) output, amphenol connectors were used. A general purpose biasing circuit was mounted inside the base. The housing can be mounted in any position. High voltage power supply was used to bias the various dynodes of the PMT. The signal output from the PMT is directly fed to the computer through interface. All the measurements were carried out in dark. All the chemicals used in the present investigation were taken in solution form and the solutions were prepared by using AR grade material adopting standard method described in the The alkaline solution of aldehydes were prepared in distilled water of different concentration. The aqueous solution of magnesium hydroxide of different concentration were prepared and tested. The concentration at which the most intense CL was obtained was selected for further investigation. The detection of CL intensity was carried out in the CL cell. The alkaline solution of aldehydes taken in the cuvette were placed in the CL cell, and finally hydrogen peroxide was injected in to the solution through syringe. For each measurement 0.5 ml of aldehydes was taken in cuvette of 0.5 ml of $Mg(OH)_2$ mixed in to it to make the alkaline

solution, then 0.5 ml of hydrogen peroxide was injected in it, otherwise mentioned in the text or graph.

RESULT AND DISCUSSION

Figure 1 shows the time dependence of CL intensity, when 0.5ml of magnesium hydroxide was mixed in 0.5ml of formaldehyde in a cuvette and finally 0.5ml of hydrogen peroxide was injected into it, in CL cell. It is clear that the CL intensity initially increases with time, attains an optimum value then decreases with further increases in time. It is also observed that the CL intensity depends on the concentration of formaldehyde and maximum CL intensity was found for formaldehyde of concentration 6%. We have also observed that the t_m (time corresponding to peak CL intensity) does not change significantly with concentration of formaldehyde and for solution of all the concentrations, the peak CL intensity occurred around 70 – 80 second.

Figure 2 shows the dependence of peak CL intensity on the concentration of different aldehydes. It is seen that the peak CL intensity initially increases with concentration, attains an optimum value for a particular concentration then decreases with further increases in concentration of aldehydes.

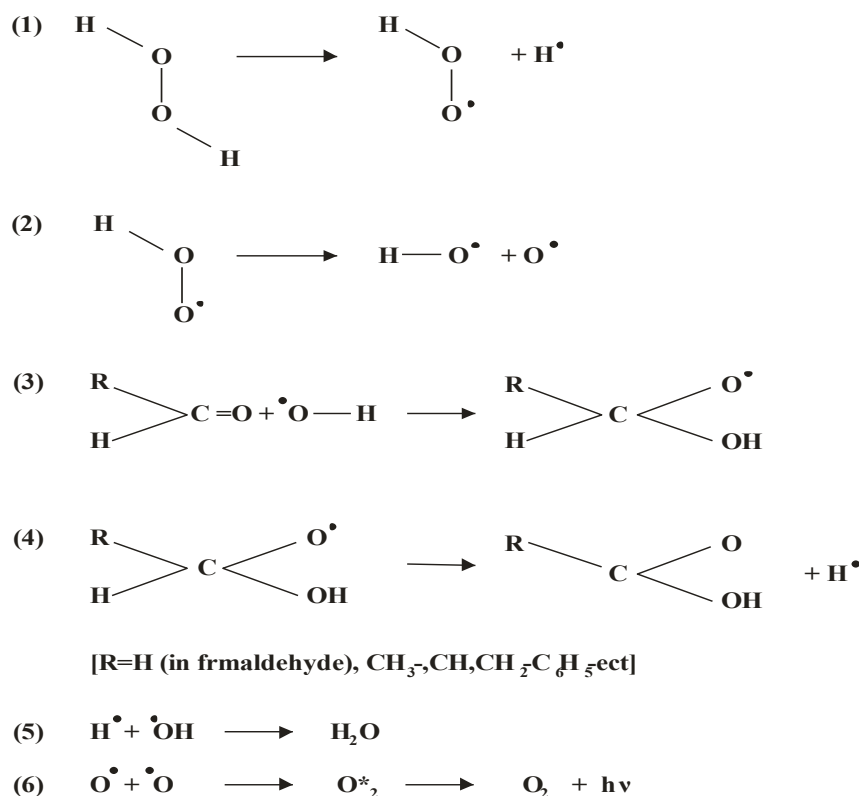
Figure 3 shows the dependence of peak CL intensity on the concentration of magnesium hydroxide. It is clear that for all aldehydes maximum CL intensity is obtained for very low concentration (0.03M) of magnesium hydroxide.

Figure 4 shows the CL reaction of acetaldehyde with hydrogen peroxide in presence of luminol. For this luminol was mixed in to this solution, it is clear that the CL intensity increases drastically and reaction becomes faster.

In the present paper the CL due to reaction between alkaline solution of aldehydes (compounds having terminal

-CHO group like formaldehyde, acetaldehyde, propionaldehyde and benzaldehyde) and hydrogen peroxide in absence and presence of luminol has been studied. The aqueous solution of aldehyde was made alkaline by $Mg(OH)_2$ and were tested for CL in absence and presence of luminol by adding H_2O_2 solution. It has been found that all the aldehydes gave strong CL (greater than as compared to alcohol) when H_2O_2 was added to their aqueous solution. This CL was highly enhanced when luminol solution was added to the above described reactions.

During the present investigation it has been observed that the reaction of aldehydes (formaldehyde, acetaldehyde, propionaldehyde and benzaldehyde) and hydrogen peroxide shows CL. The time dependence of CL intensity of the reaction, which clearly indicates that the reaction leading to light emission is quite rapid. Also by increasing the concentration of aldehydes and keeping the concentration of hydrogen peroxide constant it is observed that the CL intensity increases, which may be due to the greater production of light emitting species during the chemical reaction. The reaction of aldehydes and hydrogen peroxide produce oxygen (O_2^*) in the excited state which when return to the ground state emits light. Reaction may be summarized as above. This CL was highly enhanced when luminol solution was added to the above described reactions. The strong CL of the reaction of aldehydes in alkaline solution with H_2O_2 can be explained by easier oxidation of aldehydes to acids by H_2O_2 . The strong CL of the reaction of aldehydes in alkaline solution with H_2O_2 can be explained by easier oxidation of aldehydes to acids by H_2O_2 . A plausible mechanism of the reaction of aldehydes and H_2O_2 showing CL can be depicted using a free radical mechanism as shown below:



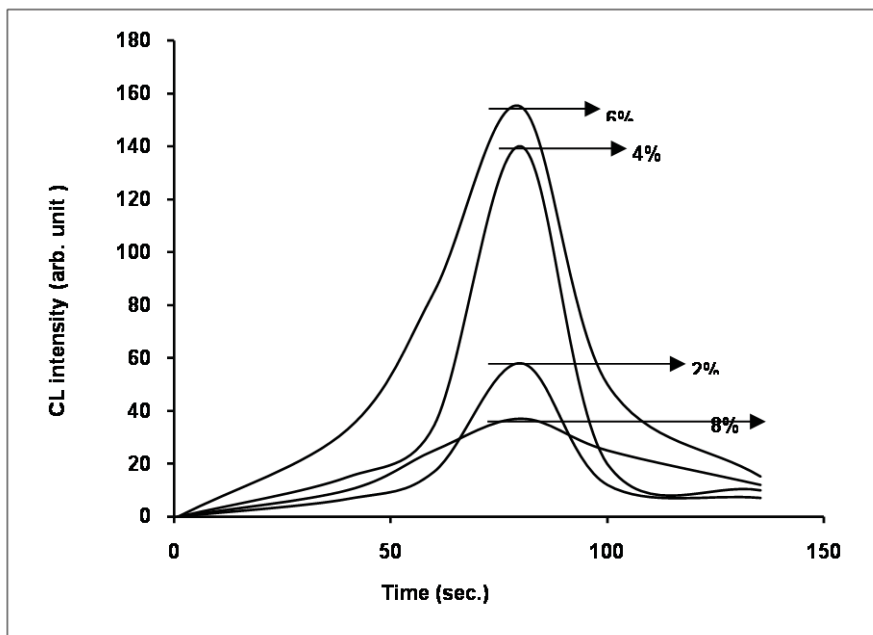


Figure 1: Time dependence of CL intensity on the concentration of formaldehyde (HCHO) under the reaction condition of 0.03M Mg(OH)₂ and 20% (w/v) H₂O₂ at room temperature.

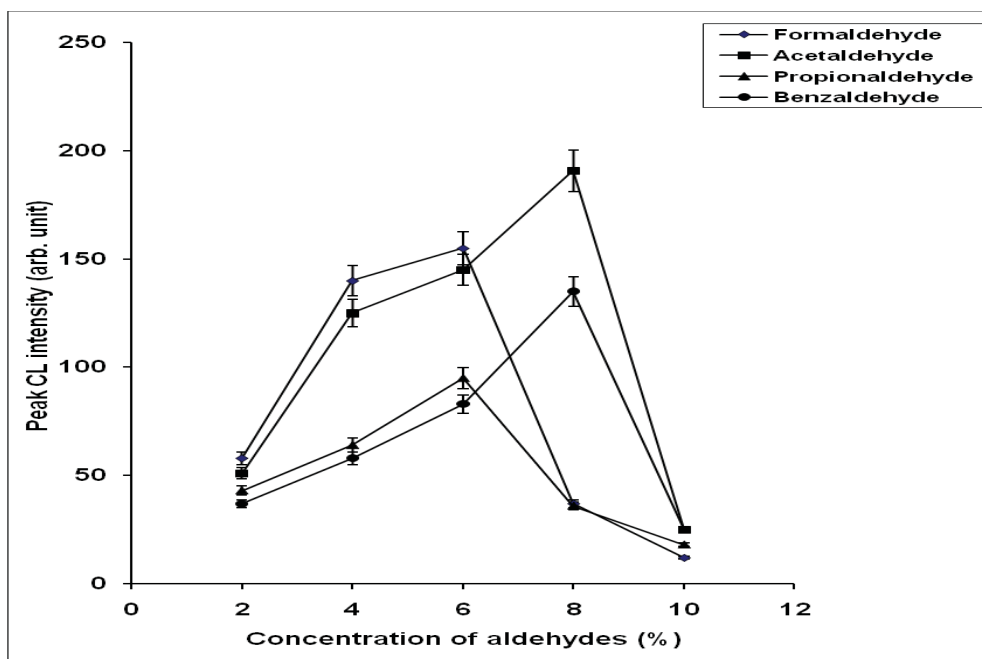


Figure2: Dependence of peak CL intensity on the concentration of aldehydes under the reaction condition of 0.03M Mg(OH)₂ and 20% (w/v) H₂O₂ at room temperature.

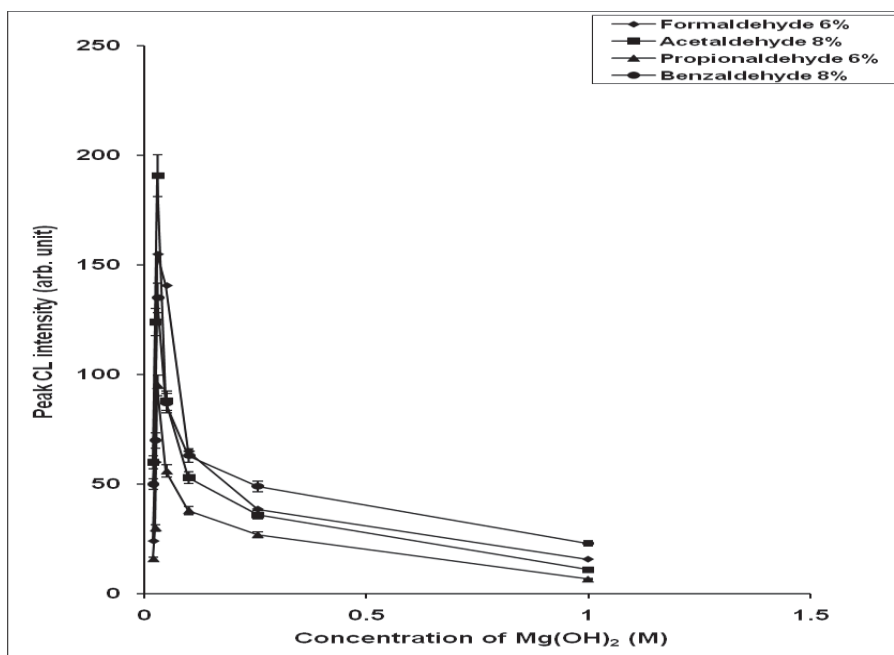


Figure 3: Dependence of peak CL intensity on the concentration of base Mg(OH)₂ under the reaction condition of aldehydes and 20% (w/v) H₂O₂ at room temperature.

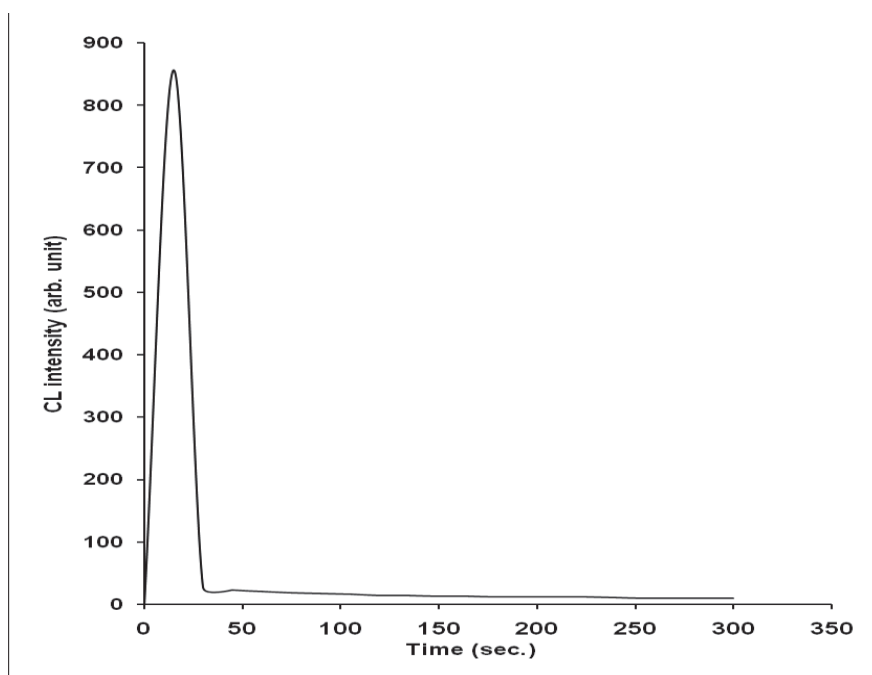


Figure 4: Time dependence of CL intensity of alkaline acetaldehyde (CH₃CHO) (8%) with hydrogen peroxide in presence of 0.001M luminol at room temperature.

CONCLUSION

From the study on chemiluminescence reactions of aldehydes (like formaldehyde, acetaldehyde, propionaldehyde, benzaldehyde) with hydrogen peroxide enhanced by luminol and the peak CL intensity was dependence of concentration of aldehydes and magnesium hydroxide. It is also found that the peak CL intensity was found alkaline acetaldehyde (CH₃CHO) (8%) with hydrogen

peroxide in presence of 0.001M luminol at room temperature. It is hoped that this study will stimulate further investigations in this field.

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