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Effect of temperature on the Chemiluminescence of alcohols and aldehydes

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Abstract

Effect of temperature on the Chemiluminescence of alcohols and aldehydes has been studied. The peak CL intensity initially increases with temperature, attains an optimum value then decreases with further increases in temperature of alcohols and aldehydes. It is also observed that maximum CL found for ethanol in alcohol group and acetaldehyde in aldehyde compound**.**

Key-Words: Temperature, Chemiluminescence, Alcohols, Aldehydes

Introduction

The Studies on the effect of temperature on luminescence properties has been interesting as it provides important information concerning the nature of the luminescent materials. It is well know fact that the chemical reactions are either kinetically or thermodynamically controlled, hence the dependence of CL on temperature is an important parameter. Most of the substances are luminescent at room temperature, but their luminesecence efficiency, is quenched at higher temperature[1]. In case of many substance which are not luminescent at room temperature shows luminescence at higher temperature[2]. Nucleosides and their polymers show CL, only at low temperature[3-4]. Obviously the dependence of luminescence intensity on temperature is extremely interesting from experimental and theoretical point of view. Shi et al. reported the temperature dependence of the CL intensity of ethanol at 425 nm. The CL signal increases with the increase in temperature from 350°C to 470°C. This was attributed to the higher conversion of ethanol into ethylene in the high temperature regions, and at low temperature ethanol mostly transformed to acetaldehyde showed that greater conversion of ethanol into ethylene at high temperature, the CL intensity has also increased[5].

From the early stage of the studies of CL, the effect of temperature on it has been the subject of great interest, because it has helped in understanding the basic mechanism of CL excitation in chemical components.

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The present paper deals with the studies on the dependence of the CL intensity on temperature of chemical reaction of alkaline alcohols (like methanol, ethanol, propanol, benzanol) and aldehydes (like formaldehyde, acetaldehyde, propionaldehyde, benzaldehyde) with hydrogen peroxide (H_2O_2).

Methodology

Assembly for CL measurements essentially consists of a chemiluminescene 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 cuvate and other for placing thermocouple in the CL cell. The cuvate 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 cuvate 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 alkaline solution of alcohols and aldehydes were prepared in distilled water of different concentration. As mentioned earlier the CL cell has the heating arrangement in it. The heater was connected to the variac. The temperature of the cell was varied by changing voltage by the variac. The temperature of the CL cell was measured by inserting a thermocouple in CL cell through the hole made on the top surface of the light tight box. To avoid the heating of the photomultiplier tube, a thick rubber sheet, with a hole at center was placed between CL cell and the photomultiplier tube housing. In order to measure the CL intensity at different temperatures the cuvate containing the solution was placed in the CL cell and the cell was heated by applying suitable voltage to the heater by a variac. The CL measurements were carried out 15 min. after the CL had attained the steady state condition. In the present investigation the temperature of the sample solution was varied from room temperature to 85°C.

Results and Discussion

The effect of temperature on the CL glow curve of reaction between methanol and hydrogen peroxide is shown in figure 1. It is clear that the CL intensity initially increases with temperature and time corresponding to CL peak shifts towards shorter time values. We have also found that the peak CL intensity attains an optimum value at 55^0C, then decrease with further increase in temperature.

The effect of temperature on the peak CL intensity of ethanol when hydrogen peroxide was injected to its alkaline solution is shown in figure 2. It has been observed that the CL intensity increases with increase in temperature attains an optimum value at 55°C then decrease with further increase in temperature.

The time dependence of the CL intensity of formaldehyde at different temperatures when hydrogen peroxide was injected into its basic solution has also been observed. It is clear from figure 3 that the peak CL intensity initially increases with time, and the time corresponding to peak CL intensity decreases with increases in temperature.

The effect of temperature on the peak CL intensity of acetaldehyde is shown in figure 4. It has been observed that the CL intensity increases with increase in temperature attains an optimum value at 55°C then further decrease with increase in temperature.

In the present investigation we have found that the CL intensity initially increase with increase in temperature attains an optimum value then decrease with further increase in temperature. Rate of reaction increases with increase in temperature and probability of radiative process may decrease with increase in temperature. Thus we expect that the CL intensity should be optimum at a particular temperature. Hence in the CL reaction of alkaline alcohols and aldehydes with hydrogen peroxide it seems that the increase in temperature lowers the energy of activation for redox CL system of alcohol and aldehyde therefore easy entropic accessible reaction enhance the CL intensity of it. After an optimum value the increase in temperature lower the energy of activation for redox CL system of alcohol and aldehyde as well as change the reaction pathway in such a manner that excitation of O_2 greatly influenced inhibit the CL intensity decrease of it.

From the study on effect of temperature on the Chemiluminescence of alcohols and aldehydes shows CL and the CL intensity initially increase with increase in temperature attains an optimum value then decrease with further increase in temperature.

Acknowledgement

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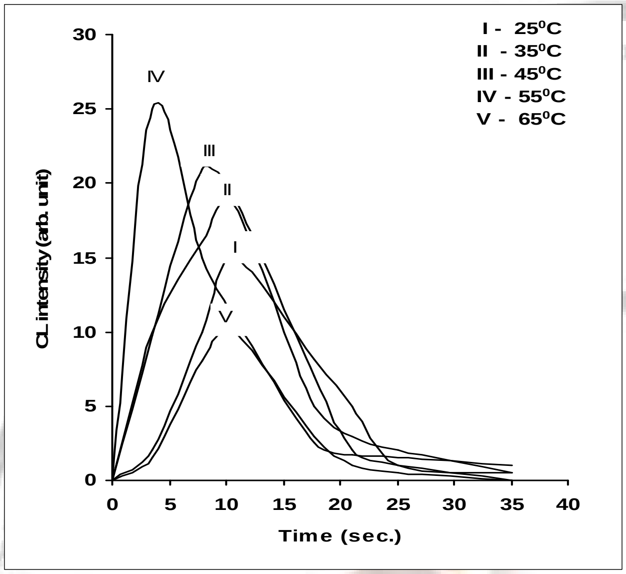

Fig. 1: Time dependence of CL intensity of methanol (CH3OH) and H2O2 at different temperature.

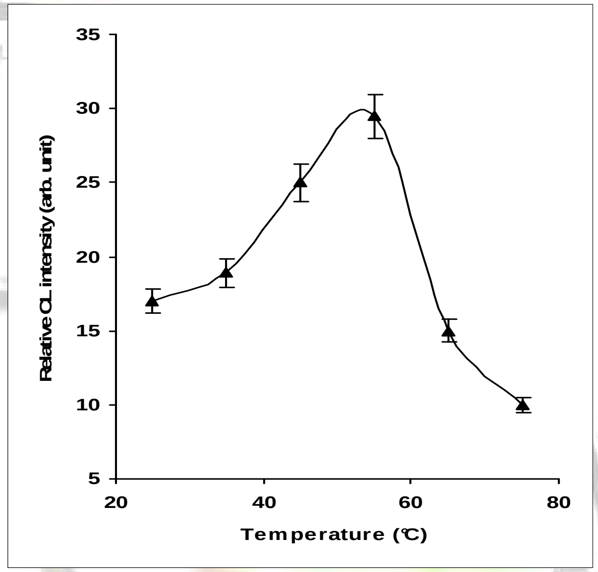

Fig. 2: Effect of temperature on the peak CL intensity for the reaction of ethanol (C2H5OH) and H2O2.

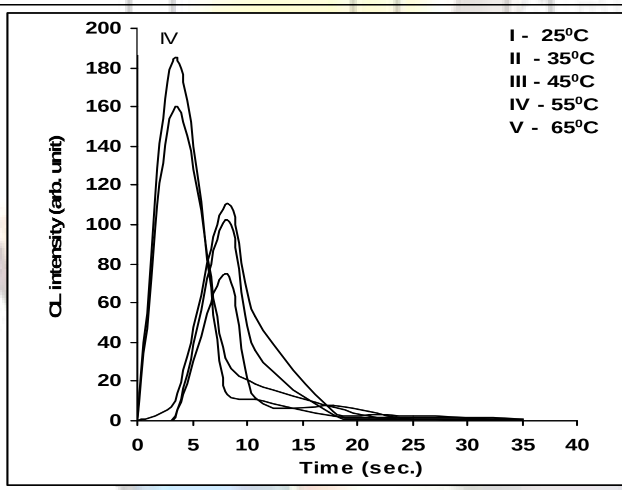

Fig. 3: Time dependence of CL intensity of formaldehyde (HCHO) and H2O2 at different temperature.

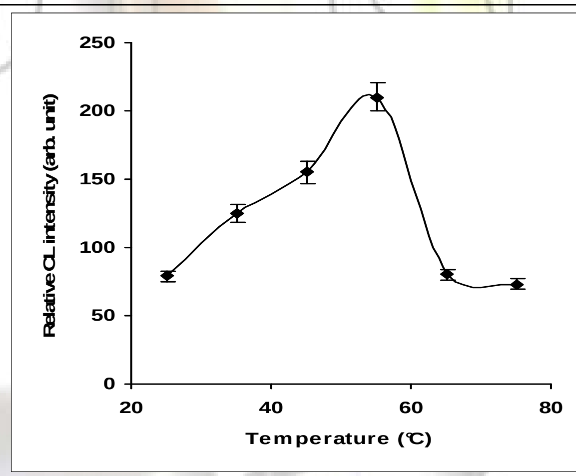

Fig. 4: Effect of temperature on the peak CL intensity for the reaction of acetaldehyde (CH3CHO) and H2O2.