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STUDY OF CHEMILUMINESCENCE BETWEEN HYPOBROMITE AND UREA

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ABSTRACT

Chemiluminescence (CL) is the process whereby energy from a chemical reaction is released directly as light without the involvement of heat or Flame. The studies of CL properties of materials are of help in exploring the rate of chemical reaction and related energy transfer process, which are generally impossible to be abstracted using other analytical tools. The main objective of the proposed investigation is to understand the mechanism of CL reaction using hypobromite and urea. Redox properties of hypobromite and urea are very important can be applied to a great variety of analytes and sample. It is possible to consider this CL method as powerful tool in analytical and environmental chemistry. Therefore it is proposed to study chemiluminescence reaction of hypobromite and urea.

Keywords- *Chemiluminescence (CL), hypobromite, urea.*

I. INTRODUCTION

Chemiluminescence (CL) is the process whereby energy from a chemical reaction is released directly as light without the involvement of heat or Flame. For decades the scientist are taking interest in the phenomenon of CL, but it has been not long as Fifteen years that significant progress were made for understanding and comprehending the chemical generation of electronically excited state which are involved in these processes. The scope of CL extended its arms in finding various significant application in the field of chemistry, physics, biology and medicine etc.

The reaction between ammonia and hypochlorite is well known due to importance in the process of disinfection of tap water and in the manufacture of hydrazine. It was reported that the reaction between hyochlorous acid and ammonia in aqueous medium the products were nitrogen trichioride, dichloramine and monuchloramine. If the solution is strongly basic, the reaction between hypochlorite and ammonia produces molecular nitrogen. Therefore this reaction was used to analyze ammonia.The reaction between hypobromite and ammonia is similar to that of hypochlorite and ammonia produces monobromamine, dibromanine and nitrogen tribromide in aqueous solution. If the solution is strongly basic, the reaction between hypobromine and ammonia produces molecular nitrogen, as in the case for the reaction between hypochlorite and ammonia .Limited numbers of investigations on the mechanism of the reaction between urea and hypochlorite or hypobromite have been reported, and it has been found that the reactions produces nitrogen in alkaline solution.

Recently, we found that the reaction between hypobromite and ammonium ion the reaction between hypobromite and urea and the reaction between hypobromite and humic acid produce light emission. The intensity for the chemiluminescence between urea and hypobromite is almost 100 times higher than that for ammonia in the same concentration with urea.

A survey of literature reveals that the reaction of ammonia and hypochlorite has been investigated in details in alkaline medium.

But limited number of investigations of the reaction between urea and hypobromite have been reported. We thought that, this technique can be applied to a great variety of analyte and sample. Therefore CL reaction between urea and hypobromite is selected for investigation.

II. EXPERIMENTAL

(i) Reagents

Hypobromite solution was prepared by diluting commercially available hypobromite solution with distilled water. The concentrations of hypobromite was measured by the thiosulfate iodide titrimetric method. Urea solution was

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prepared by dissolving urea into distilled water. Sodium hydroxide was prepared by diluting standard solution of sodium hydroxide solution. All chemicals used were AR grade.

(ii) Apparatus and Procedure

Assembly for CL measurements essentially consists of a chemiluminescence cell, high voltage power supply, light detector, digital multimeter (scientific SM 5015) and PC . A window was made on one side wall of the CL cell in front which the photomultiplier type was placed to detect the light coming through the window which is produce during the chemical reaction. The CL cell and photo multiplier 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 chemical in the cuvate and other for placing thermocouple in the CL cell. The cuvate is fitted inside the top surface of light tight box and it rest just below the circular hole in which the syringe is placed. The cuvate is a highly transparent glass 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 PMT housing used for CL measurement is made of thick soft iron to provide a shielding form light. The slit arrangement at the window was provided for adjustment of the size of the window according to the 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 was directly fed to digital multimeter (scientific SM 5015) interfaced with PC. The detection of CL intensity was carried out in the CL call. The solutions of different components were injected in the CL cell through syringe for each measurement required volume of different components were take as it mentioned in the text or graph. The CL due to reaction was detected by the PMT and recorded on PC through digital multimeter.

In the present investigation CL spectra were recorded by placing band pass filter between the windows of the chemiluminescence *cell and* the PMT (RCA 931) of the set. The output of the PMT was fed to the PC through interface. Rest of the arrangements and chemicals same as described before. Different filters were placed between the window of the CL cell and PMT and the observations were recorded on a PC linked through interface. The CL intensity was normalized for the different transmission coefficient of the filter. For CL spectra at least three observations were taken for each filter. All the measurements were carried out in dark.

III. RESULTS & DISCUSSION

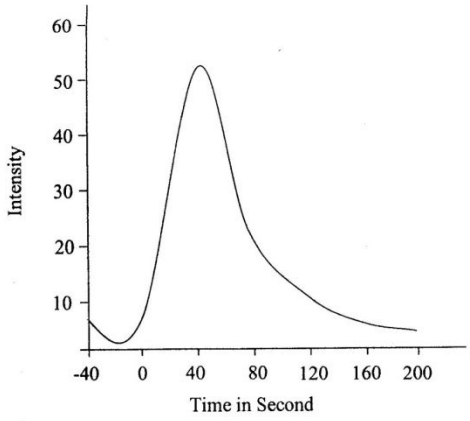

Fig. 1-Time dependence CL intensity of Urea, 0.03 mol dm1, sodium hypobromite, 0.02 mol dm^{-1}; sodium hydroxide, 0.1mol dm^{-1}

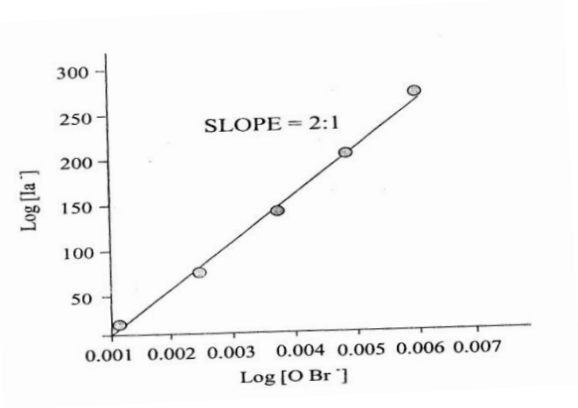

Fig.2- Relation between CL intensity and hypobromite concentration is in excess. Sodium hydroxide 0.1 mol dm^{-1}; Urea, 0.025 mol dm^{-1}

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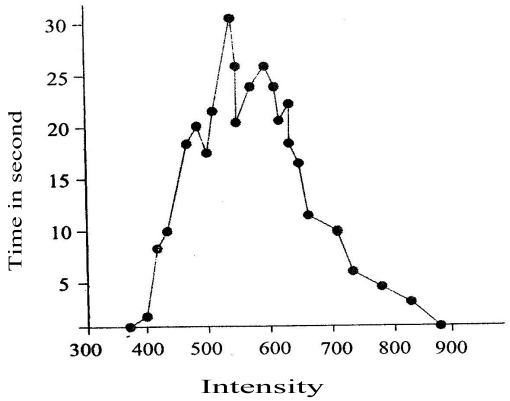

Fig.3- Relation between CL intensity and hypobromite concentration when urea concentration is in excess.

Sodium hydroxide 0.1 mol dm^{-1}; Urea, 0.025 mol dm^{-1}

i) Time dependence chemiluminescence intensity

The time dependence of CL intensity of reaction between hypobromite and urea solution in alkaline media is shown in fig. 1. The reaction was carried out in the presence of base. It is evident form figure that the chemiluminescence intensity initially increases linearly with time, attains an optimum value and then decreases with time.

ii) Relation between CL intensity and the reactant concentration

The relationship between the chemiluminescence intensity and the reactant concentrations was investigated using the flow injection analysis system. Results show that the chemiluminexcence intensities relate to the concentrations of urea by second order when hypobromite is in excess of urea. On the other hand, on average, the chemiluminescence intensity shows second order on the concentration of hypobromite when urea is in excess of hypobromite. An experimental result for the urea reaction is shown in fig. 2. This suggest that the rate of formation of the emimmion species for the reaction of hypobromite with urea obeys second order kinetic with respect ot hypobromite concentration.

iii) Chemiluminescence spectra

The chemiluminescence spectrum of the reaction of 0.2 mol dm'^{1} Hypobromite, 0.2 mol'^{1} urea containing 0.2 mol dm'^{1} sodium hydroxide are shown in fig. 3.The spectrum of the chemiluminescence produced by urea reaction shows a broad band from 400 to 700 nm with a structure. The maximum emission of urea was at 510 nm.

iv) Tentative scheme of the chemiluminescence reaction

For the reaction of hypobromite and urea, molecular nitrogen is reported as potential candidate. Nitrogen is known to have a visible emission in the wavelength region longer than 337 nm(18) accompanied by a structure resulting from vibrational progressins. We could not resolve the structure in the chemiluminescence from the reaction between hypobromite and urea due to the poor resolution of the spectrometer used in this study. Therefore, although the spacing of the structure must be identified to assign the emission species, nitrogen is the probable species for the emission species. According to the discussion above, we tentatively propose the scheme for the chemiluminescence reaction as follows:-

Reaction between urea and hypobromite

$$(NH_2)_2CO + 2OBr^- \rightarrow N_2^* + 2Br^- \quad \ldots\ldots(1)$$

$$N_2^* \rightarrow N_2^* + h\nu \quad \ldots\ldots(2)$$

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