



EFFECT OF SOLVENT ON THE INTENSITY OF CHEMILUMINESCENCE PRODUCED DURING DECOMPOSITION REACTION BETWEEN LUMINOL AND HYDROGEN PEROXIDE

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Abstract

The Chemiluminescence properties of luminol were studied in various protic and aprotic solvents with different dielectric constants. It was observed that CL-behavior like I_{\max} , t_{\max} , τ_1 and τ_2 depend largely on hydrogen bonding of CL-species with the solvent molecule, resulting changes in CL-behavior to occur due to difference in transition probability.

Keywords : *Chemiluminescence, Luminol, Hydrogen Peroxide, Solvent effect*

1. Introduction

Chemiluminescence (CL) and bioluminescence (BL) are natural phenomena which have attracted the attention of mankind since the evolution of life on the earth. CL based on the oxidation of luminol (LH_2) (5-amino-2,3-dihydro-1,4-phthalazinedione) is one of the most extensively studied and best known CL system [1-3]. The oxidation is usually carried out in an alkaline solution using an oxidant such as hydrogen peroxide [4], hypochlorite [5], permanganate [6], or iodine [7]. The luminol- H_2O_2 system is one of the most efficient CL systems known to date. The reaction is catalyzed by peroxidases [8], metal ions [9], or metal containing species [10-11]. Luminol-CL in water is mostly applied for analytical purposes, in special forensic medicine (to detect trace amounts of blood); this is why luminol reaction in water has been intensely investigated. The CL of the system luminol-DMSO has several practical applications [12], so it is also useful to know more about the spectroscopic behavior of this system. The luminol CL in different solvents and solvent mixtures are much less studied, although some reports on the fluorescence behavior of this system have appeared in last few years [13, 14]. In the present paper, the effect of some solvents on the decomposition reaction between luminol and hydrogen peroxide is reported.

2. Experimental details

2.1 Materials :

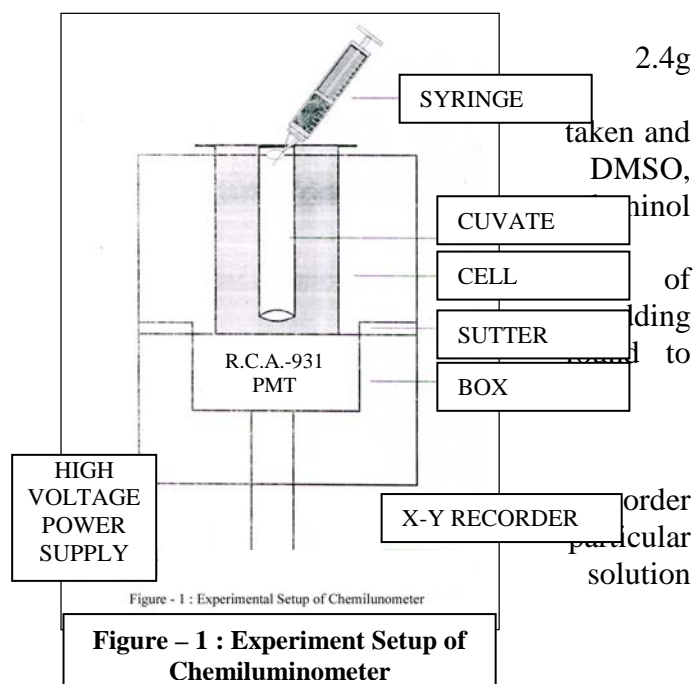
The solvents dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF) and acetonitrile (AN) (all from E merch, AR/GR grade) used were of spectroscopic grade and were further distilled before use. Triple distilled water was used throughout during the studies. Luminol (from Thomas backer), anhydrous sodium carbonate, sodium bicarbonate, ammonium carbonate monohydrate, copper(II) sulphate pentahydrate, hydrogen peroxide (all from E merch, AR/GR grade) were used.

2.2 Solutions preparation :

For the present investigation, 0.01g luminol, NaHCO_3 , 0.4g Na_2CO_3 (anhydrous), 0.05g $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$, 0.04g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were dissolved in 100 ml of the solvent (water, DMF and AN). This was the stock solution of with respect to particular solvent. For the preparation of 1.5% H_2O_2 stock solution, taken 30% H_2O_2 solution and made up into 100ml by studying solvent (the actual H_2O_2 content was be by titration against KMnO_4).

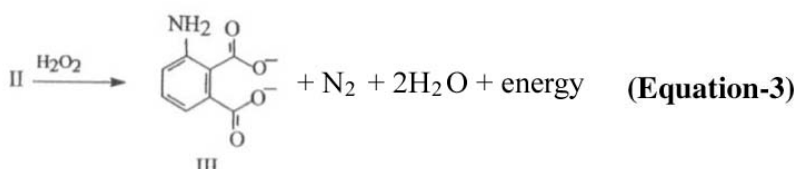
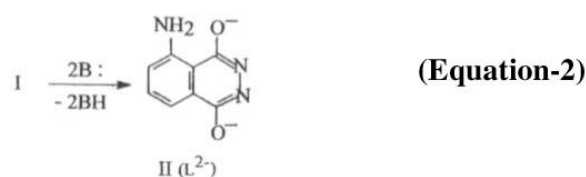
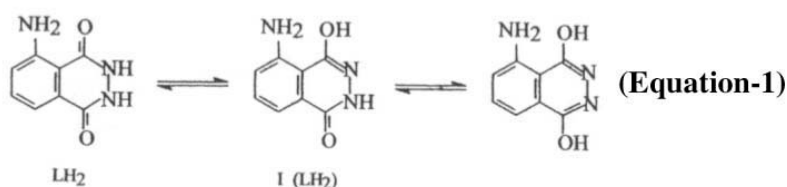
2.3 Instruments and Methods :

All the experiments were performed on a chemiluminometer setup connected to a X-Y (Fig.1). Stock solution of luminol (1ml) in solvent was taken in reaction cell and H_2O_2 (1ml) was added through syringe.

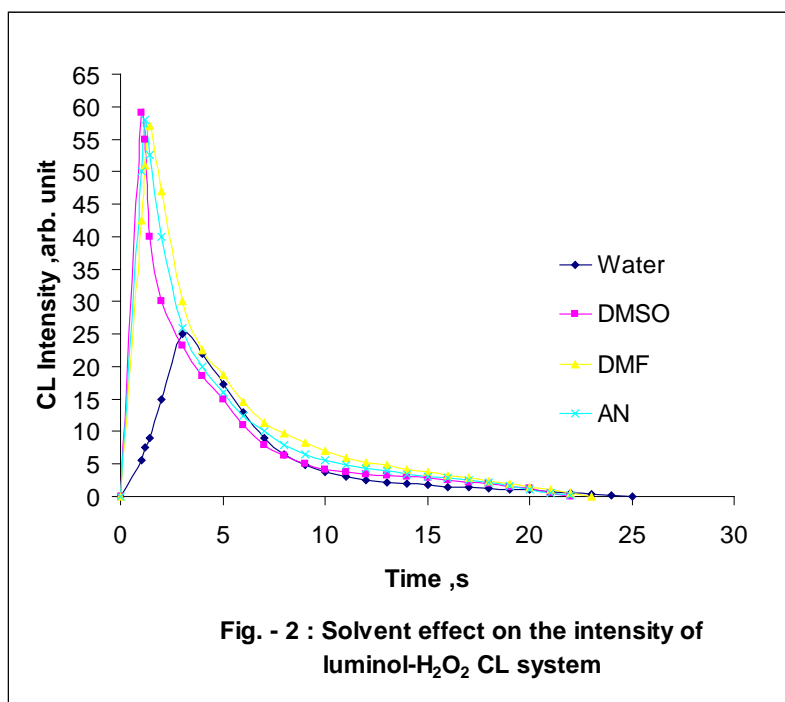


3. Results and Discussion

The structure of luminol (Eq.1) confers acidic properties, so in presence of a base there results the dianionic species L^{2-} is formed (Eq.2), which on oxidation with hydrogen peroxide yields the 3-Aminophthalate dianion (III) along with release of reaction energy (Eq.3). This energy is absorbed by species III and which forms the excited state (Eq.4) and then returns to ground state with CL emission (Eq.5).



Reaction scheme I



clear that I_{\max} is minimum when solvent is water (protic). Protic solvent like water can interact more with CL species in ground state than excited state, therefore large energy gap occurs between these energy states and so its intensity is less and decay time is more. In aprotic solvent (DMSO, DMF, AN etc.), interaction between solvent molecules and CL species is less (some interaction may be due to the presence of water), so transition probability is more in these solvents and intensity is more than in protic solvent (water). From Table-1, it is seen that t_{\max} is more for protic solvent than in aprotic solvent. It seems that in protic solvent hydrogen bonding interaction between solvent molecule and CL species is more, therefore time required for maximum intensity t_{\max} is also more than that for aprotic solvent. Reaction rate of this system is also affected by the solvent used, which is evidence from Table-1.

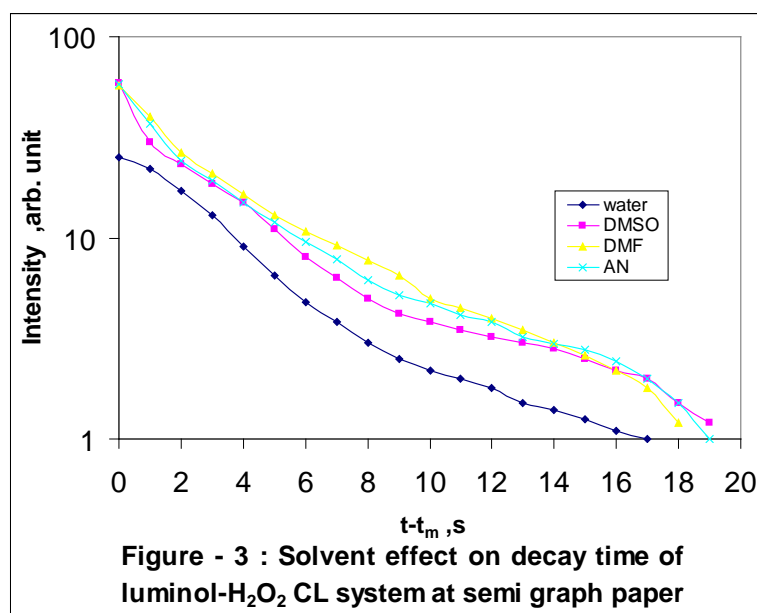
4. Conclusions

From the study on luminol- H₂O₂ CL behavior involving the effect of solvents (H₂O, DMSO, DMF and AN), the important conclusions drawn are:

- Luminol CL depends largely on hydrogen bonding with the solvent molecules.
- In protic solvents like water, CL intensity is less due to smaller transition probability.
- In aprotic solvents like DMSO, DMF, AN, etc., CL intensity is more due to higher transition probability.
- Position of t_{\max} is affected by the solvent used.

It has long been known that spectroscopic behavior of chemical compounds may be influenced by the surrounding medium and so the solvents can bring about a change in the position, intensity, and shape of absorption and emission bands. In CL-reactions, solvent may affect the released energy and after that fluorescent species (by stabilization and de-stabilization interaction).

Fig. 2 and 3 and Table-1 show the solvent effect on the maximum intensity I_{\max} , time at maximum intensity t_{\max} , fast decay slope M_1 , slow decay slope M_2 , fast decay time τ_1 and slow decay time τ_2 of luminol-H₂O₂ system. From the Table, it is



(iv) Reaction rate depends on the solvent used.

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Table – 1 : Effect of solvent on the luminol- H_2O_2 CL system

Solvent	I_{\max} , arb. unit	t_{\max} , s	M_1 , s^{-1}	M_2 , s^{-1}	τ_1 , s	τ_2 , s
Water	25.0	3.0	0.2742	0.1116	3.6469	8.9606
DMSO	59.0	1.0	0.3104	0.1155	3.2221	8.6561
AN	58.0	1.2	0.3151	0.1269	3.1735	7.8787
DMF	57.0	1.4	0.2953	0.1448	3.3865	6.9056

I_{\max} = Maximum Intensity, t_{\max} = Time at maximum intensity, M_1 = Fast decay slope, M_2 = Slow decay slope, τ_1 = Fast decay time, τ_2 = Slow decay time.

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