ISSN : 0974 - 7486 Volume 8 Issue 5

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 8(5), 2012 [187-192]

1, 4-Dihydroxyanthraquinone (Quinizarin) in tetrahydrofurane reacts as a novel chemiluminescence reagent in a peroxyoxalate - System

Abdollah Yari*, **Marzieh Saidikhah**

Department of Chemistry, Faculty of Science, Lorestan University, Falakalaflak Street 68178-17133, Khorramabad, (IRAN)

E-mail : a.yari@ymail.com

Received: 25th October, 2011 ; Accepted: 25th November, 2011

ABSTRACT

In this work, we investigated the chemiluminescence generated from the reaction of bis(2,4,6-trichlorophenyl)oxalate (TCPO), hydrogen peroxide and 1,4-dihydroxyanthraquinone (quinizarin). Furthermore, the effect of solvent and concentrations of necessary reagents, TCPO, sodium salicylate, hydrogen peroxide and quinizarin on the luminescence efficiency of the system were studied. Under the optimal condition the suitable values of concentrations of the TCPO:H_2O_2:SS:Qz system were of 5.50×10^{-4}, 8.34×10^{-2}, 4.27×10^{-6} and 7.51×10^{-4} M, respectively.

KEYWORDS

Chemiluminescence;
Enhancing effect;
Peroxyoxalate;
Quinizarin.

INTRODUCTION

Chemiluminescence (CL) is the generation of electromagnetic radiation (ultraviolet, visible or infrared) by a chemical reaction without any changing in temperature. There are two types of CL reactions: direct CL and indirect or sensitized CL. Direct CL is the CL reaction in which electronically excited intermediate emits light but in indirect CL this intermediate transfers its energy to a fluorophore that can luminescence subsequently[1, 2]. The most efficient non-enzymatic indirect chemiluminescence reaction with quantum efficiency up to 50% is peroxyoxalate chemiluminescence (PO-CL) system. In 1963 Chandross, for the first time, observed bluish-white light from a mixture of oxalyl chloride, hydrogen peroxide and 9.10-diphenylanthracene in 1,4-dioxane as a solvent[3, 4]. PO-CL reaction can be used for direct or indirect detection of hydrogen peroxide (produced by enzymatic reaction), determination of ionic compounds, fluorophore and fluorescent derivatized compounds. In addition, PO-CL technique will be highly selective when coupled with some techniques such as capillary electrophoresis (CE) and high performance liquid chromatography (HPLC)[5-13].

Quinizarin (Qz) is an orange crystalline powder, which is a good fluorogenic agent for detection of some metallic ions or can be used for their simple spectrophotometric determinations. Qz has various properties such as being a fungicide, pesticide or using as a dye, a photoinitiator or an additive in lubricants[14-17]. Trying to discover a correct structure for Qz has been a basis for many researches[18-20]. As shown in Figure 1, Qz has three tautomeric structures[21].

In the current work, the chemiluminescence of the reaction between TCPO and hydrogen peroxide in the presence of Qz, as fluorophore, has been investigated. In addition, the system showed an enhancing effect in

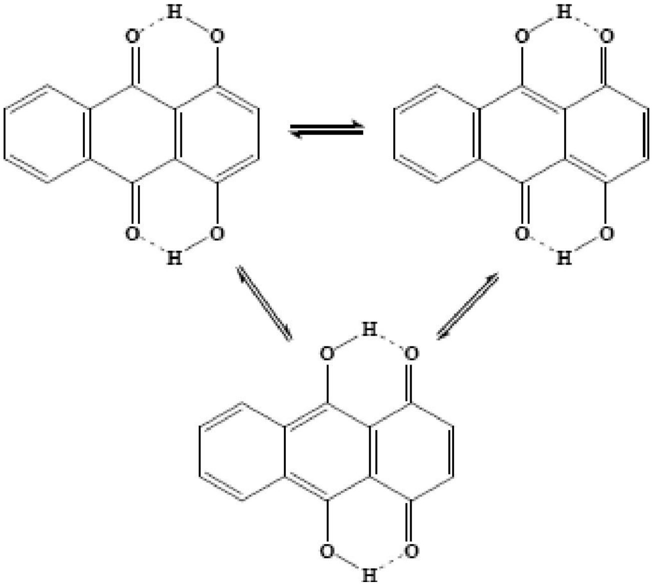


Figure 1 : The tautomeric structures of 1,4- dihydroxyanthraquinone (Quinozarin).

the presence of aluminum(III) ion. We are investigating this enhancing effect and the results are demonstrated in our next work.

EXPERIMENTAL

Materials and apparatus

Commercial reagents were obtained from Merck and used without further purification. TCPO synthesized from the reaction of 2,4,6-trichlorophenol and oxalyl chloride in the presence of triethylamine as described elsewhere[22]. The chemiluminescence spectra and all emission intensities were recorded by using a Varian Cary Eclipse fluorescence spectrophotometer.

Procedure

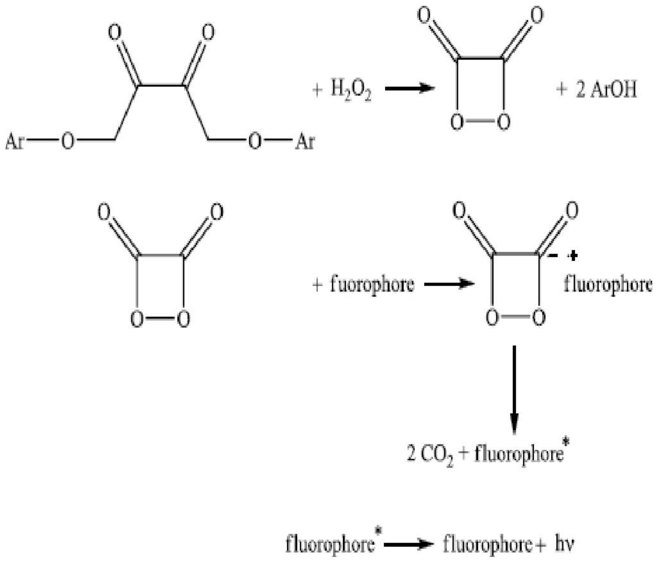
At room temperature, proper amounts (□L) of stock solutions of hydrogen peroxide (in acetonitrile), TCPO (in ethyl acetate) and SS (in methanol) was added to a 1 cm quartz cell containing 1.5 mL (9.51×10^{-4} M) of Qz (in THF), and the CL (a.u.) spectra of the mixture were recorded immediately. All solutions were freshly prepared when they were used in the measurements.

RESULTS AND DISCUSSION

As we could find in the literature, the familiar proposed mechanism for PO-CL reaction is as demonstrated in scheme 1. According to them, a chemically initiated electron exchange luminescence (CIEEL) mechanism is responsible of the excitation. It has been shown that a key intermediate, 1,2-dioxetanedione (DOD), a highly strained and unstable molecule, is produced in this mechanism[4, 23-28]. DOD forms a charge transfer complex with a fluorophore by accepting one electron from fluorophore and then a chemiluminescence light emits after the decomposition of this complex. As seen in the following steps, in an indirect CL fashion, when hydrogen peroxide reacts with oxalate ester (here TCPO), after an intramolecular displacement, DOD is formed but this resulted molecule will not emit light and transfers its energy to the fluorophore (Qz, in this work) by producing two CO_2 molecules. Afterward the resulting sensitized fluorophore releases its energy in the form of light or heat[23, 29-31].

$$2TCPO + H_2O_2 \xrightarrow{k_1} C_2O_4 + 2HTCP \qquad (1)$$

$$C_2O_4 + QNZ \xrightarrow{k_2} [C_2O_4^{\bullet -} QNZ^{+-}] \qquad (2)$$



Scheme 1 : The proposed mechanism for the PO–CL reaction.

$$[C_2O_4^{\bullet -} QNZ^{+-}] \xrightarrow{k_3} QNZ^* + 2CO_2 \qquad (3)$$

$$QNZ^* \xrightarrow{k_4} QNZ + hv \qquad (4)$$

or

$$QNZ^* \xrightarrow{k_5} QNZ + heat \qquad (5)$$

Optimization of experimental factors

Experimentally, we saw an intense bright orange

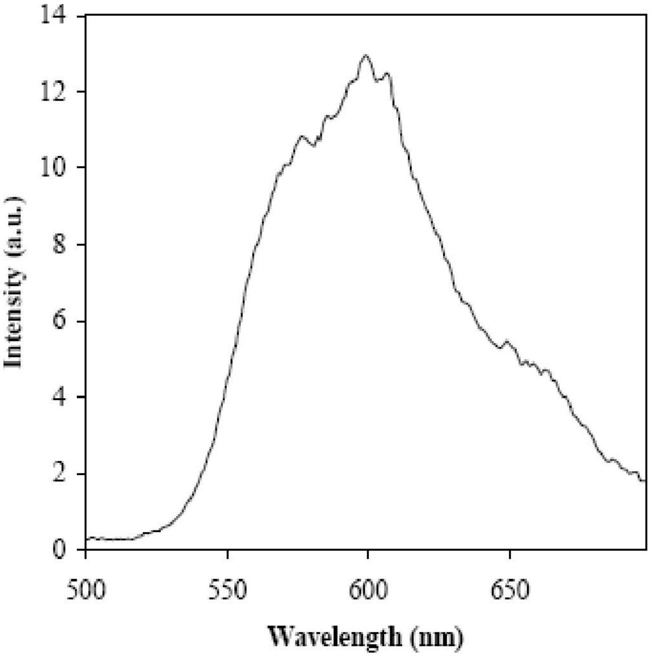


Figure 2 : The Chemiluminescence emission spectra of Qz (1.91×10^{-2} M).

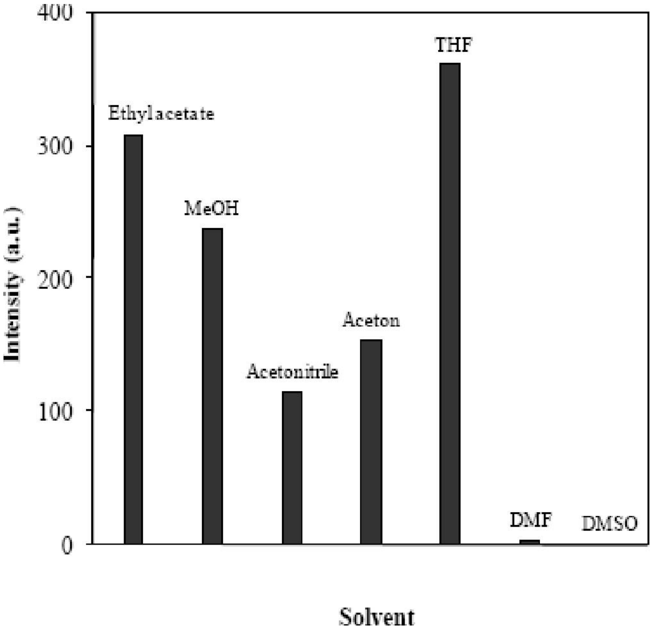


Figure 3 : The effect of the type of solvent on the chemiluminescence intensity of the PO–CL/Qz system; Qz (7.51×10^{-4} M), TCPO (5.50×10^{-4} M), SS (4.27×10^{-4} M) and H_2O_2 (8.34×10^{-2} M).

light with a long lifetime immediately after the addition of hydrogen peroxide to the mixture of TCPO, SS and Qz. The chemiluminescence emission spectra of Qz are shown in Figure 2. As it is obvious from this Figure, the system has shown its maximum of emission at wavelength of about 600 nm.

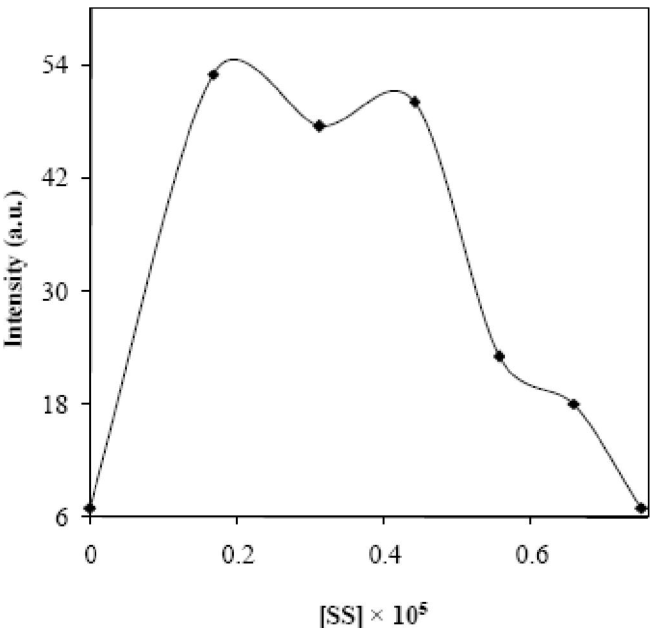


Figure 4 : The effect of SS concentration (0.00 to 7.50×10^{-6} M) on the PO–CL system in the presence of Qz (7.51×10^{-4} M), TCPO (5.50×10^{-4} M) and H_2O_2 (8.34×10^{-2} M), respectively.

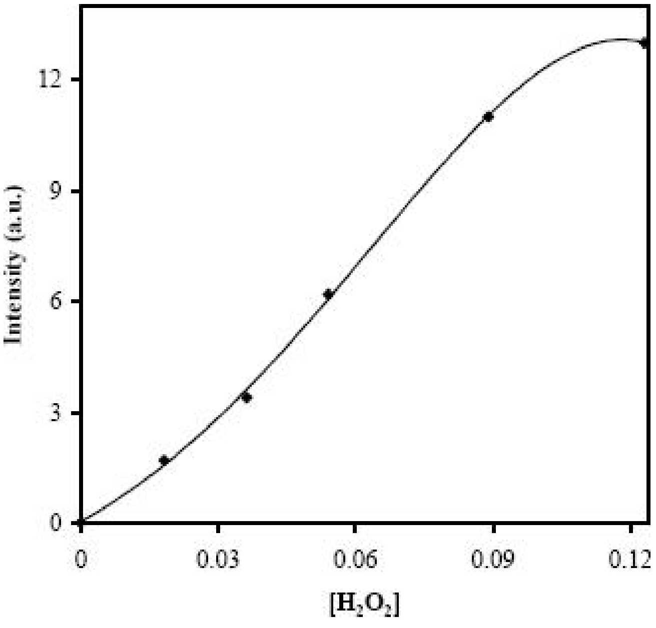


Figure 5 : The effect of H_2O_2 concentration (0.00 to 0.12 M) on the chemiluminescence intensity of Qz (7.51×10^{-4} M) in the presence of TCPO (5.50×10^{-4} M) and SS (4.27×10^{-6} M).

We have already expected the crucial effect of the kind of the solvent in which the CL reagents react[32]. The effects of various types of solvents on the intensity of PO–CL were examined. Figure 3 shows the effects of some common solvents including ethylacetate, methanol (MeOH), acetonitrile, aceton, tetrahydrofurane

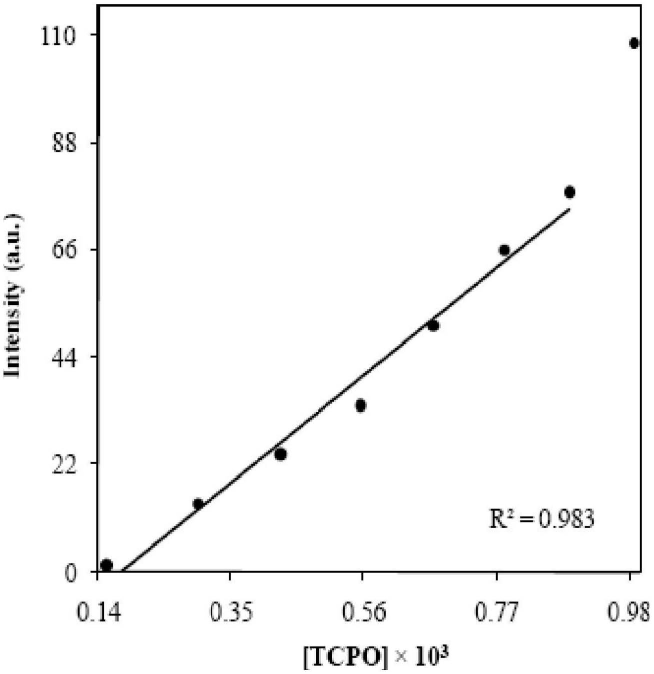


Figure 6 : The influence of varying concentrations of TCPO (1.45×10^{-4} to 9.84×10^{-4} M) in the system containing H_2O_2 (8.34×10^{-2} M), SS (4.27×10^{-6} M) and Qz (7.51×10^{-4} M).

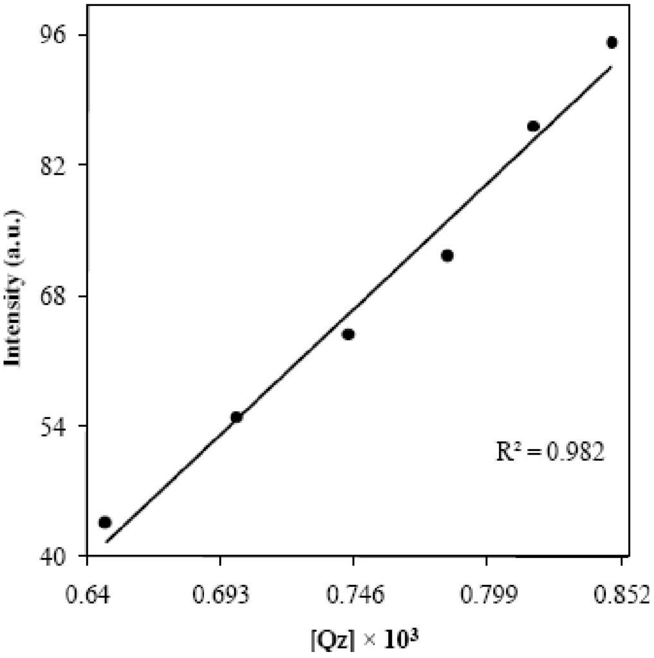


Figure 7 : The effect of Qz concentration (6.47×10^{-4} to 8.48×10^{-4} M) on the CL intensity in the presence of the TCPO:H_2O_2:SS system with concentrations of 5.50×10^{-4}, 8.34×10^{-2} and 4.27×10^{-6} M, respectively.

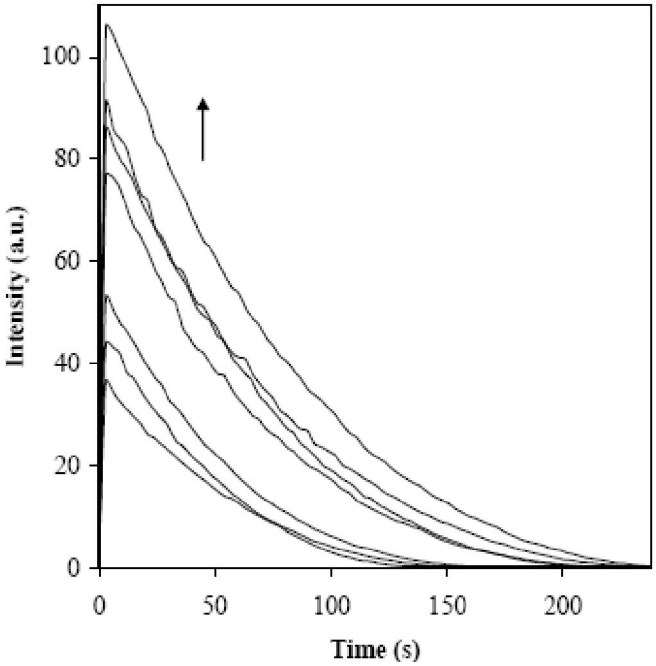


Figure 8 : The CL intensity-time plots of the optimized Qz–TCPO–H_2O_2–SS system were obtained by changing the concentrations of Al^{3+} ions.

(THF), dimethylformamide (DMF) and dimethysulfoxide (DMSO) on the intensity of PO–CL system when the concentrations of all reagents were kept fixed. We found that THF was the best solvent for the PO–CL system of Qz.

Another factor that must have been checked for the PO–CL/Qz system was the effect of SS concentration, as the CL catalizer agent. After addition of SS to the system, the intensity of the emitted light increased while a weak signal had been emitting before the addition of SS. As shown in Figure 4, the increase in the intensity of the light raised until the concentration of SS reached 1.67×10^{-6} M. CL intensity was nearly constant in the concentration range of 1.67×10^{-6} to 4.41×10^{-6} M of SS beyond that the quenching effect of SS on CL intensity started. The resulted evidence confirms that the catalytic role of SS had been responsible of the increasing in CL signal and the later decrease in the CL intensity could have been due to the decomposition of the key intermediate 1,2-dioxetanedione[29]. Thus, we used optimal concentration 4.27×10^{-6} M of SS for the subsequent studies.

In Figure 5, the effect of H_2O_2 concentration is demonstrated. As seen, there is no emitted CL light in the absence of H_2O_2 in the test solution, which is indicative the oxidant role of H_2O_2[33]. From this Figure, there is a linear relationship between the intensity of CL and the concentration (less than 0.1 M) of H_2O_2. Thus, 8.34×10^{-2} M of H_2O_2 was used as optimal concentration in further experiments.

In order to find the relationship between the concentrations of TCPO and Qz and the intensities of the emitted CLs from the tested system[34], the CL of the system were plotted against the concentrations of TCPO and Qz in the solution separately. The results are shown in Figures 6 and 7. As seen in Figure 6, the plot shows a linear behavior with increasing amounts of TCPO concentration from 1.45×10^{-4} to 9.84×10^{-4} M. The 5.50×10^{-4} M of this range was selected as the fixed TCPO concentration in all experiments. Furthermore, from the linear plot shown for Qz (6.47×10^{-4} to 8.48×10^{-4} M) in Figure 7, 7.51×10^{-4} M was used as useful concentration of Qz in the solution.

Finally, from the fact that Qz can form a complex with Al^{3+} ion[15, 35], we are investigating the CL of the proposed system in the presence of Al^{3+} in the solution. From the primarily experiments we found that Al^{3+} ion is a good enhancing reagent for the PO–CL system of Qz. Figure 8 indicates the CL intensity–time plots of Qz–TCPO–H_2O_2–SS system, which were obtained by addition of various concentrations of Al^{3+} ions to the solution. We are going to publish the results as soon as possible.

CONCLUSION

As shown by the results obtained in this investigation, we can say that quinizarin could be used as an actual fluorophore in the chemiluminescence emission reaction of a peroxyoxalate system. Quinizarin can transfer the sensitization energy of the system and give it up as a clear intense bright orange light with a long lifetime. On the other hand, quinizarin is able to form complex(s) with metal ions such as aluminum(III). So it can be used as a chemiluminescence chemosensor for selective determination of some species in the solution, which will be described in our next work.

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