A Study of Chemiluminescence from Reaction of Bis(2,4,6-trichlorophenyl)oxalate–H_2O_2 in the Presence of a Novel Blue Fluorescer, Furandicarboxylate Derivative

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Abstract: The chemiluminescence (CL) arising from the reaction of bis(2,4,6-trichlorophenyl)oxalate (TCPO) with H_2O_2 in the presence of a novel blue fluorescer, furandicarboxylate derivative, has been studied. The relationship between the CL intensity and concentrations of peroxyoxalate, sodium salicylate, H_2O_2 and furandicarboxylate derivative as fluorescer has been investigated. Kinetic parameters for the peroxyoxalate chemiluminescence (PO-CL) including intensity at maximum CL, time at maximum intensity, total light yield, theoretical maximum level of intensity and pseudo-first-order rate constants for the rise and fall of the CL burst (k_r and k_f) were also calculated from the computer fitting of the corresponding CL intensity/time profiles. It was found that the furandicarboxylate derivative can be used as an efficient blue fluorescent emitter.

1. Introduction

Chemiluminescence (CL) is a phenomenon in which an electronically excited molecule is generated during the chemical reaction and emits light as a visual output. Owing to the advantages of high sensitivity, wide linear range, simple instrumentation, and fast dynamic response, CL has continually received more and more attention in the last years [1-3]. CL has been used in various fields, including environmental, biological, clinical, food, and pharmaceutical analysis [4].

Of the numerous CL reactions known to date, peroxyoxalate chemiluminescence (PO-CL) is the most effective one (quantum yield up to 50%), which

has been extensively investigated since its discovery by Chandross [5]. A typical PO-CL consists of the reaction of the active oxalates, such as bis(2,4,6-trichlorophenyl)oxalate (TCPO), H_2O_2 as oxidant and a catalyst, in which light emits from the excited states of various externally added fluorescent activators [6]. In the peroxyoxalate system, 1,2-dioxetanones [7] including a 1,2-dioxetanedione [8, 9] and some cyclic peroxides [10] have been suggested as the high energy key intermediates capable of producing an excited species by their thermal decomposition according to a chemically initiated electron exchange luminescence (CIEEL) process [11-13].

In this paper, we report the study of CL from the reaction of TCPO and H_2O_2 with the laboratory-synthesized diethyl 2-(*tert*-butylamino)-5-biphenyl-3, 4-furandicarboxylate (as shown in the scheme 1) as an efficient fluorescence brightener, in the presence of sodium salicylate as a base catalyst. The furan derivative is an intense and useful fluorescer compound containing an aromatic functional group with a low energy $\pi \rightarrow \pi^*$ transition level and a rigid structure (blue light emission).

The influence of TCPO, H_2O_2, and sodium salicylate concentration on the intensity, decay and duration of CL emission systems in the presence of the fluorescer has been studied in a great detail. Kinetic parameters for the PO-CL were also calculated from the computer fitting of the corresponding CL intensity/time profiles.

2. Experimental

2.1. Chemicals and solutions

All chemical compounds were reagent-grade and purchased from Fluka chemical company (CH-9470, Buchs, Switzerland) and used as received without further purification. The furandicarboxylate derivative **4** was synthesized and purified in our laboratories, as described before [14]. We described in detail the preparation of polyfunctionalized furan ring by reaction of alkyl isocyanides **1** with dialkyl acetylenedicarboxylate **2** in the presence of trans-cinnamaldehyde **3**. This three component reaction produces highly functionalized furan **4** in fairly good yields. The yield of reaction for production of the furan derivative was about 65% (Scheme 1).
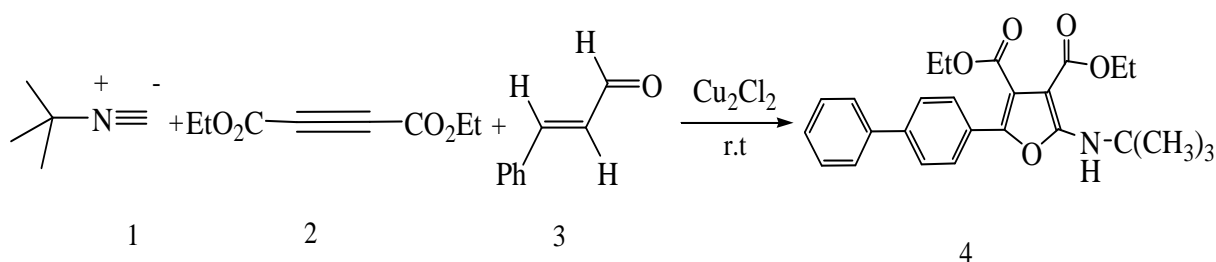
Scheme 1. Synthesis of di(ethyl)-2-(*tert*-butylamino)-5-biphenyl-3,4-furandicarboxylate.

2.2. Chemiluminescence measurements

Chemiluminescence detection was performed with a homemade apparatus equipped with a model BPY47 photocell (Leybold, Huerth, Germany). The apparatus was connected to a personal computer via a suitable interface (Micropars, Tehran, Iran). Experiments were carried out with magnetic stirring (500 rpm) in a light-tight flattened bottom glass cell of 15 mm diameter at room temperature. The fluorescence spectra were recorded with a Perkin Elmer, Ls50 spectrofluorimeter instrument.

2.2. Procedures

Solution *I* was made by mixing 1.0 mL of TCPO (0.01 M) and 0.5 ml of fluorescer (various concentrations in ethyl acetate) and 1.5 mL of ethyl acetate. Solution *II* contained 2 mL of H_2O_2 (4 M) and 1.0 mL of sodium salicylate (0.1 M) in methanol. Solution *I* was transferred into the instrument quartz

cuvette via polypropene syringes. Then 100 µL of solution *II* was injected into the quartz cuvette and the CL profile was recorded after mixing as soon as possible.

3. Results and discussion

The peroxyoxalate system is the only chemiluminescent reaction supposed to involve an intermolecular CIEEL mechanism with proven high quantum yields [13, 15, 16]. This system consists of a base-catalysed reaction of activated oxalic phenylesters with H_2O_2 in the presence of highly fluorescent aromatic hydrocarbons with low oxidation potentials as chemiluminescent activators. The mechanism of PO-CL process has been postulated to involve at least one highly energetic intermediate(s) (possibly a dioxetane species) capable of exciting a fluorescent receptor molecule [13, 17], as shown in scheme 2.
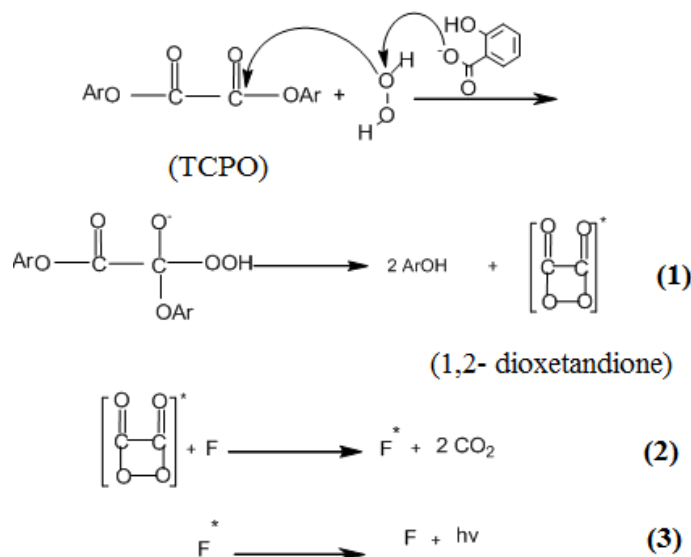
Scheme 2. Generally accepted understanding of the CIEEL mechanism in PO–CL.

It is well known that a base catalyst is needed to improve the reactivity of TCPO. The most frequently employed, imidazole and sodium salicylate act as a base catalyst for the deprotonation of H_2O_2 [13, 15]. According to this mechanism, in the first step, sodium salicylate promotes the formation of the hydroperoxy anion (HOO^-), a stronger nucleophile than H_2O_2, then TCPO reacts with HOO^- to produce a key chemical intermediate of 1,2- dioxetandione (C_2O_4) as an excitation source. The second step, excited cyclic C_2O_4 intermediate transfer its energy to fluorescer (F, here furandicarboxylate derivative was used as fluorescer), resulting in an excited fluorescer (F^*). The final step is the emission of light energy by returning the excited fluorescer molecule to the ground state.
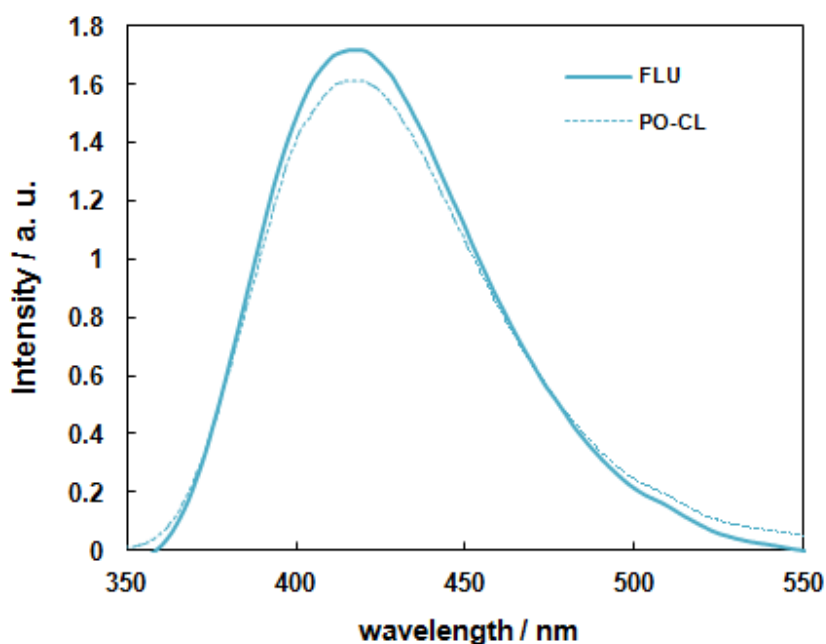

Fig. 1. Steady state fluorescence (solid line), and chemiluminescence (dashed line) spectra of the furandicarboxylate derivative (1.0×10^{-3} mol dm^{-3}).

The sensitized PO-CL spectrum of fluorescer together with its emission spectrum is shown in Fig. 1. As it is apparent, since the light emission steps for both CL and fluorescence are essentially analogous, the emission wavelength maxima in both processes are similar (*i.e.*, 420 nm).

In order to evaluate the kinetic data for the PO-CL system, a pooled intermediate model was used [10, 18]. According to this model, the CL reaction is simplified as:

$$A \xrightarrow{k_r} B \xrightarrow{k_f} C \qquad (1)$$
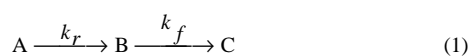
where A, B and C represent pools of reactants, intermediates and products, respectively, and both reaction steps designated by the rate constants k_r and k_f are irreversible first-order reactions. The integrated rate equation for the CL intensity versus time is:

$$I_t = [\frac{Mk_r}{k_f - k_r}][\exp(-k_r t) - \exp(-k_f t)] \qquad (2)$$

Where I_t is the CL intensity at time t, M is a theoretical maximum level of intensity if the reactants were entirely converted to a CL-generating material, and k_r and k_f are the first-order rate constants for the rise and fall of the burst of CL, respectively. A further advantage of this model is that it not only allows the determination of parameters M, k_r and k_f, but also it permits an estimate of the intensity at maximum level (J), the time of maximum

intensity (T_{max}) and the total light yield (Y), as follows:

$$J = M(\frac{k_f}{k_r})^{[k_f/(k_r - k_f)]}$$

(3)

$$T_{max} = \frac{\ln(k_f/k_r)}{k_f - k_r}$$
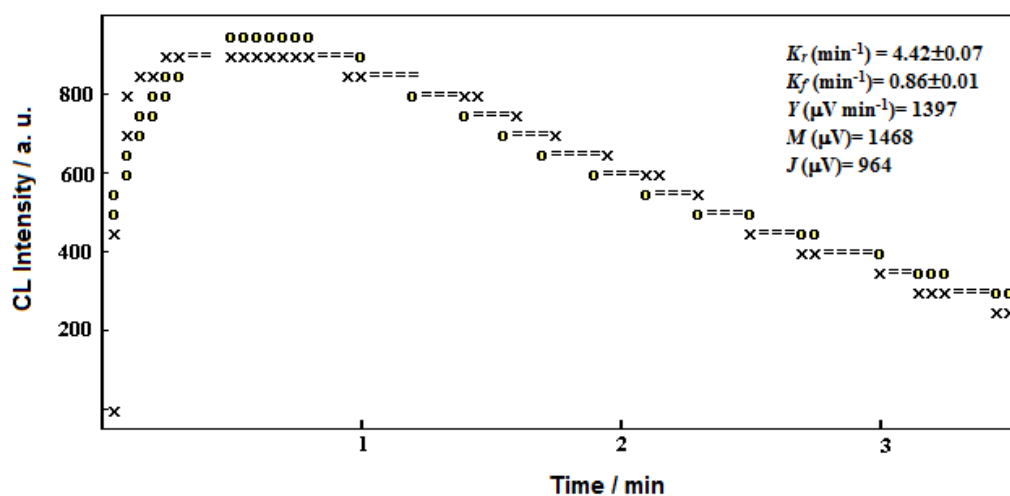
(4)

$$Y = \int_0^\infty I_t dt = \frac{M}{k_f}$$

(5)

Fig. 2. A typical computer fit of the CL intensity–time plot for TCPO–H_2O_2–fluorescer–sodium salicylate system (H_2O_2, 5.1×10^{-2} mol dm^{-3}; sodium salicylate, 1.2×10^{-3} mol dm^{-3}; fluorescer, 1.6×10^{-4} mol dm^{-3} and TCPO, 1.6×10^{-3} mol dm^{-3}): ($\times$) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plot.

In this work, a non-linear least-squares curve fitting program, KINFIT [19] was used to evaluate the M, k_r and k_f values from the corresponding CL intensity–time plots. A typical computer fit of the CL intensity time plots is shown in Fig. 2. The theoretical values of maximum intensity (J), and corresponding time (T_{max}) and Y can be calculated by Eqs. 3, 4 and 5 using parameters of k_f, k_r and M which were determined from the resulting CL intensity-time plots. All kinetic parameters are listed in Table 1. The

experimental values of maximum intensity (I_{max}) and T_{max} were extracted from CL intensity-time plots.

Fig. 3 shows CL intensity as a function of time (intensity/time emission profile) for the PO-CL system in the presence of varying concentrations of TCPO. As is obvious from the inset of Fig. 3 there is a nice linear correlation between the CL intensity and the TCPO concentration. The basis for such linear correlation has already been discussed in literature [20, 21].

It is interesting to note that both the rate constants k_r and k_f are more or less independent of TCPO concentration (within the experimental errors), as it is the limiting reagent in the CL process (Table 1).

Such constancy of k_r and k_f with increasing TCPO concentration confirms that the reaction is pseudo first-order in TCPO when H_2O_2 is present in large excess [10]. Fig. 4 shows CL intensity as a function of time for the PO-CL system in the presence of varying concentrations of fluorescer. As it has been clearly shown before [20], there is an exponential increase in CL of the H_2O_2-TCPO-fluorescer system with increasing concentration of the fluorescer, in the concentration range studied. However, the reciprocal plot of CL intensity against fluorescer resulted in a linear calibration graph (Fig. 4).
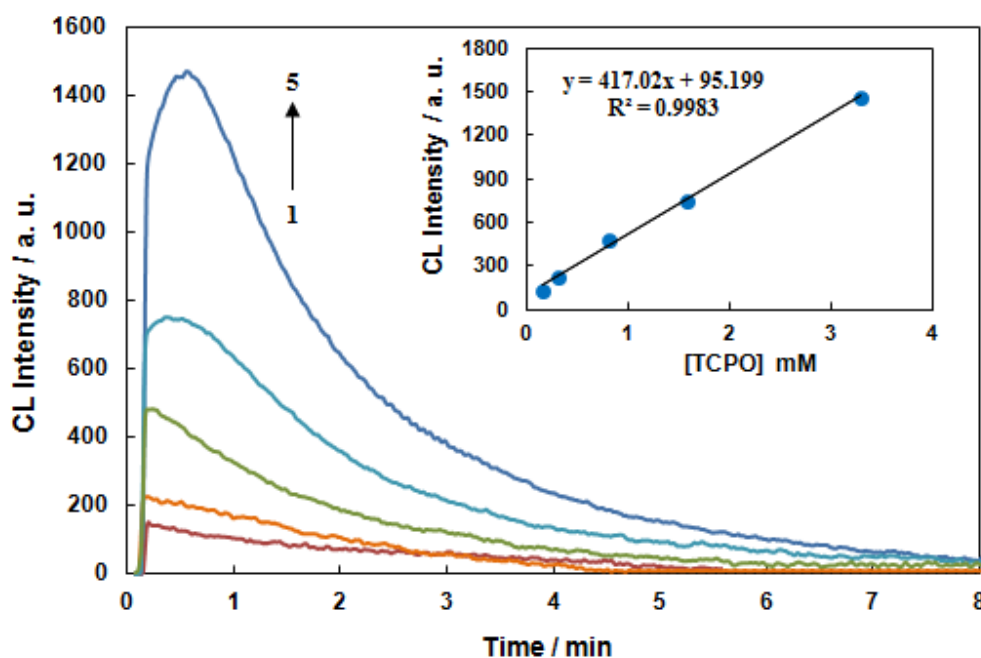

Fig. 3. CL intensity as a function of time for reaction of H_2O_2 (5.1×10^{-2} mol dm^{-3}), sodium salicylate (1.2×10^{-3} mol dm^{-3}) and fluorescer (1.6×10^{-4} mol dm^{-3}) in ethylacetate in the presence of varying concentrations of TCPO: (1) 1.7×10^{-4}, (2) 3.3×10^{-4}, (3) 8.3×10^{-4}, (4) 1.6×10^{-3}, (5) 3.3×10^{-3} mol dm^{-3}. Corner of right hand side: correlation diagram for the CL emission with TCPO concentrations.

Table 1 reveals that although the rate constants k_r and k_f obtained for the PO-CL reaction are more or less independent the fluorescer concentration, the CL total yield increases with increasing fluorescer concentration, which is consistent with previous reports [20, 22]. Such observations declare the fact that the high-energy cyclic intermediates (*i.e.*, dioxetane species) may transfer energy to a fluorescer via the CIEEL mechanism.

Table 1. CL parameters evaluated from computer fitting of the CL intensity–time plots for TCPO- H_2O_2 - furandicarboxylate derivative – sodium salicylate system.

Parameter changed	Concentration (mol dm^{-3})	k_r (min^{-1})	k_f (min^{-1})	M (µV)	J_{exp} (µV)	J (µV)	T_{exp} (min)	T_{max} (min)	Y (µV/min)
TCPO	1.7×10^{-4}	8.0±0.4	0.42±0.06	151.4±2.2	141	128	0.31	0.38	360
	3.3×10^{-4}	8.2±0.3	0.47±0.01	253.5±2.5	224	213	0.21	0.26	539
	8.3×10^{-4}	5.1±0.2	0.64±0.02	574.1±11.1	481	457	0.26	0.30	897
	1.6×10^{-3}	4.5±0.1	0.57±0.09	1061.1±9.2	753	728	0.49	0.50	1861
	3.3×10^{-3}	3.6±0.1	0.67±0.02	2104±24.0	1468	1429	0.59	0.57	3140
H_2O_2	1.7×10^{-2}	1.4±0.09	0.20±0.06	256.1±2.1	120	132	0.79	0.74	1423
	3.3×10^{-2}	2.4±0.09	0.26±0.02	393.5±4.9	380	321	0.75	0.67	1711
	5.1×10^{-2}	4.0±0.12	0.34±0.08	1013.3±11.2	771	790	0.61	0.63	2980
	6.7×10^{-2}	5.3±0.11	0.49±0.03	1710.5±18.9	1217	1248	0.46	0.46	3491
	8.4×10^{-2}	5.4±0.13	0.50±0.03	1920.3±21.9	1300	1428	0.43	0.40	3729
Sodium salicylate	4.0×10^{-4}	2.5±0.8	0.45±0.06	1253.4±9.4	921	955	0.79	0.77	2785
	8.0×10^{-4}	3.6±0.5	0.58±0.01	1707.5±19.8	1144	1094	0.77	0.74	2944
	1.2×10^{-3}	4.1±0.5	0.58±0.07	1812.4±12.7	1277	1237	0.64	0.61	3125
	1.6×10^{-3}	4.2±0.6	0.64±0.13	1891.2±6.3	1213	1182	0.60	0.57	2955
	2.0×10^{-3}	4.2±0.8	0.65±0.15	1756.3±6.5	1122	1002	0.58	0.57	2850
fluorescer	1.7×10^{-5}	2.7±0.1	1.08±0.38	260.8±7.5	157	143	0.51	0.55	241
	8.3×10^{-5}	2.9±0.2	1.51±0.08	1009.7±50.3	591	500	0.42	0.46	669
	1.6×10^{-4}	1.6±0.1	1.60±0.07	1704.6±10.6	669	627	0.91	0.86	1065
	4.2×10^{-4}	2.1±0.1	0.66±0.03	1773.5±52.1	1052	1044	0.81	0.80	2687
	8.3×10^{-4}	2.5±0.1	1.51±0.01	1725.6±28.6	1130	1150	0.81	0.80	3383
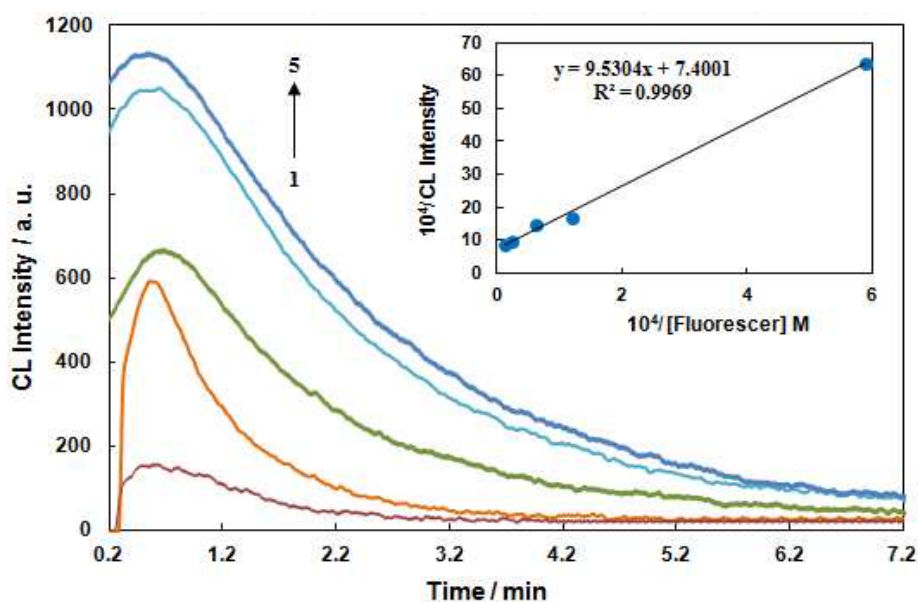
Fig. 4. CL intensity *vs*. fluorescer concentration with H_2O_2 (5.1×10^{-2} M) in the presence of sodium salicylate (1.2×10^{-3} M) and TCPO (1.6×10^{-3} M), in ethyl acetate: (1) 1.7×10^{-5}, (2) 8.3×10^{-5}, (3) 1.6×10^{-4}, (4) 4.2×10^{-4}, (5) 8.3×10^{-4} mol dm^{-3}. Corner of right hand side: The bireciprocal plot of CL emission with fluorescer concentrations.

Previous kinetic works has shown that the charge-transfer steps leading to CL are fast relative to the formation of an initial intermediate and, for this reason, the final reactions leading to CL are kinetically unobservable [20-24].

The influence of H_2O_2 concentration on the PO-CL was studied at constant concentration of other reagents and presented in Fig. 5 and Table 1. It was found that there is a direct linear relationship between the concentration of H_2O_2 and PO-CL intensity of the system, at the concentration ranges of 1.7×10^{-2}-6.7×10^{-2} mol dm^{-3}. However, further increase in H_2O_2 concentration (i.e., $6.7 \times 10^{-2} >$ mol dm^{-3}) was found to have no significant effect on the PO-CL intensity. Even though, in the absence of sodium salicylate, I_t at each H_2O_2 concentration was found to be much lower than that in the presence of the salt. The observed behavior is clearly indicative of the catalytic effect of sodium salicylate on the PO-CL system studied [25-27].
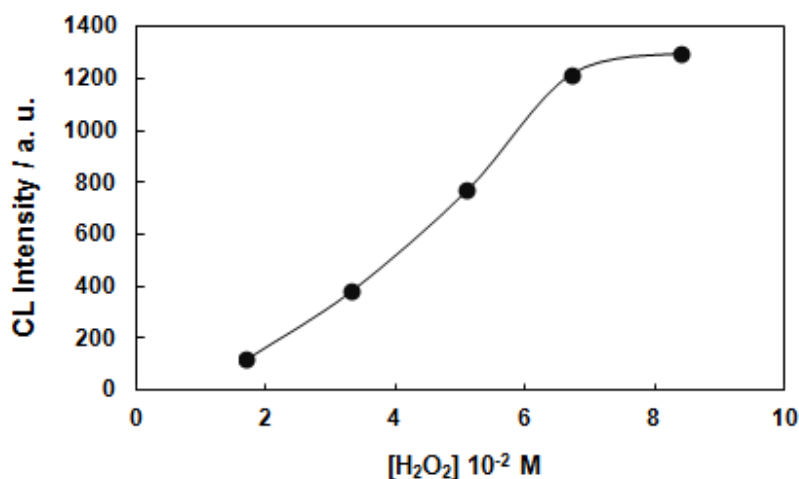

Fig. 5. Effect of H_2O_2 concentration on the CL intensity of TCPO-H_2O_2- fluorescer system. TCPO (1.6×10^{-3} mol dm^{-3}), sodium salicylate (1.2×10^{-3} mol dm^{-3}) and fluorescer (1.6×10^{-4} mol dm^{-3}) in ethylacetate in the presence of varying concentrations of H_2O_2: (1) 1.7×10^{-2}, (2) 3.3×10^{-2}, (3) 5.1×10^{-2}, (4) 6.7×10^{-2}, (5) 8.4×10^{-2} mol dm^{-3}.

It is interesting to note that, with the excess amount of H_2O_2, the pseudo-first-order fall rate constant, k_f, increases linearly with increasing H_2O_2 concentration with a regression equation $k_f = 0.095[H_2O_2] + 0.085$ (Table 1) with a relatively large intercept of about 0.085 min^{-1}, which is representative of a first-order reaction that is zero-order in concentration of H_2O_2 [10, 28]. Meanwhile, the pseudo-first-order rate constant for the rise step k_r increased linearly with increasing H_2O_2 concentration (Table 1). In this case, the linear plot of k_r vs. H_2O_2 concentration passes through the origin, within the experimental error, which is consistent with the previously reported mechanism proposed by Hadd et al. for the PO-CL reactions in the organic media [10]. The intensity/time emission profile of furandicarboxylate derivative, under the optimal constant concentrations of TCPO, H_2O_2 and flourescer indicated that the emission intensity is significantly enhanced by addition of sodium salicylate. This confirms a key role of

catalyst in the PO-CL system. In order to investigate the optimal concentration of sodium salicylate, the CL response of the H_2O_2-TCPO-fluorescer system was measured against the varying concentrations of the sodium salicylate the resulting plot is shown in Fig. 6.As seen, the PO-CL intensity rapidly increased with increasing concentration of sodium salicylate until a concentration of 1.2×10^{-3} mol dm^{-3} is reached. However, further addition of sodium salicylate causes to decrease the CL intensity and in total yield, Y (Table 1). This, probably due to the quenching effect of the base at higher concentrations, which possibly it leads to decompose the intermediate, dioxetanedione, and hence reduces the PO-CL light [26-30].
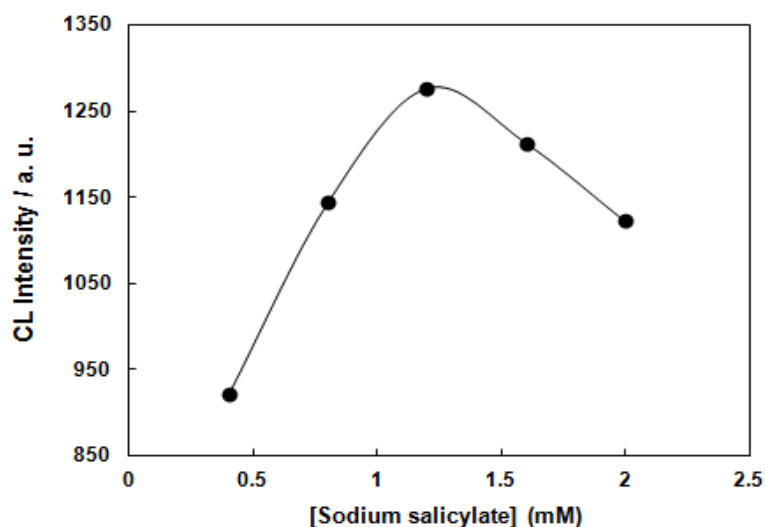

Fig. 6. Effect of sodium salicylate concentration on the CL intensity of TCPO-H_2O_2- fluorescer system. TCPO (1.6 $\times$ 10^{-3} M), H_2O_2 (5.1×10^{-2} M) and fluorescer (1.6×10^{-4} M) in ethylacetate in the presence of varying concentrations of sodium salicylate: (1) 4.0×10^{-4}, (2) 8.0×10^{-4}, (3) 1.2×10^{-3}, (4) 1.6×10^{-3}, (5) 2.0×10^{-3} mol dm^{-3}.

4. Conclusion

The present study describes a new CL system of H_2O_2- bis-(2,4,6-trichlorophenyl) oxalate (TCPO) using furandicarboxylate derivative as fluorescer. In this system, a blue light is produced in the present of furandicarboxylate derivative. The results indicated how concentrations of the components involved in CL, influence on the light emission. Kinetic parameters for the PO-CL of fluorescer were calculated from the corresponding CL intensity-time plots. A non-linear least-squares curve fitting program, KINFIT was used to evaluate the theoretical maximum level of intensity (*M*), the first order rate constants for the rise k_r and fall k_f of the burst of CL. The furandicarboxylate derivative is found intense and useful fluorescer compound which produces blue light emission.

5. References

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