A Study of Chemiluminescence from Reaction of Bis(2,4,6-trichlorophenyl)oxalate, Hydrogen Peroxide and Diethyl-2-(cyclohexylamino)-5-[(E)-2-phenyl-1-ethenyl]-3,4-furandicarboxylate as a Novel Fluorescer

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The chemiluminescence (CL) arising from reaction of bis(2,4,6-trichlorophenyl)oxalate (TCPO) with hydrogen peroxide in the presence of a diethyl-2-(cyclohexylamino)-5-[(E)-2-phenyl-1-ethenyl]-3,4-furandicarboxylate as a novel fluorescer (Flu) has been studied. The relationship between the chemiluminescence intensity and concentrations of TCPO, sodium salicylate, hydrogen peroxide and fluorescer is reported. The chemiluminescence parameters 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 evaluated from computer fitting of the resulting intensity-time plots. The activation parameters E_a, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ for the rise and fall steps were evaluated from the temperature dependence of k_r and k_f values.
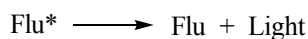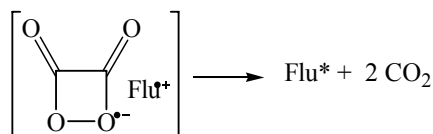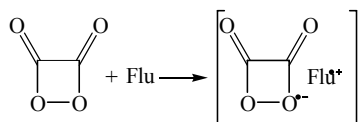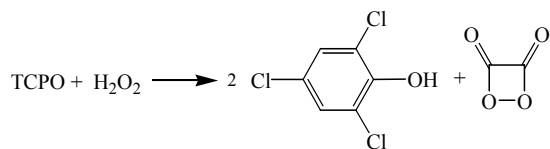
INTRODUCTION

Peroxyoxalate chemiluminescence (PO-CL) is well known as a powerful technique for the sensitive and some times selective determination of a large variety of analytes, depending on the roles they play in the CL reaction as fluorophores [1-4], catalysts [5], quenchers [6-8], oxidants [9,10], *etc*. In principal, PO-CL involves hydrogen peroxide oxidation of an aryl oxalate ester in the presence of a fluorophore (activator). Although the reaction mechanism of PO-CL is still under controversy, it has been suggested that

the reaction follows a chemically initiated electron exchange luminescence (CIEEL) mechanism *via* the formation of high energy intermediate(s) such as 1,2-dioxetanedione [11,12,]. These meta stable intermediates form complexes with the fluorophore that donates one electron to the intermediate [13,14]. This electron is transferred back to the fluorophore raising it to an excited state and liberating light characteristics typical for the fluorophore nature. This phenomenon is typically depicted in Scheme 1.

Although several authors have investigated the kinetics and mechanism of the PO-CL reaction, the key pathway(s) and nature of the reactive intermediate(s) remain highly uncertain and the intermediate(s) were never directly observed.

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$$TCPO + H_2O_2 \longrightarrow 2 \; \text{Cl} \underset{\text{Cl}}{\overset{\text{Cl}}{\bigcirc}} OH + \underset{O-O}{\overset{O \quad O}{\square}} \tag{1}$$

$$\underset{O-O}{\overset{O \quad O}{\square}} + Flu \longrightarrow \left[\underset{O-O^-}{\overset{O \quad O}{\square}} Flu^+ \right] \tag{2}$$

$$\left[\underset{O-O^{\bullet-}}{\overset{O \quad O}{\square}} Flu^+ \right] \longrightarrow Flu^* + 2 \; CO_2 \tag{3}$$

$$Flu^* \longrightarrow Flu + Light \tag{4}$$

Scheme 1

Dioxetanedione was first suggested by Rauhut *et al.* as a reaction intermediate [15] and then aryl-containing dioxetane derivatives and six-member intermediate(s) were proposed by other researchers [11,16,17,18]. Appearance of different mechanisms and intermediates for PO-CL in the literature reactions is a result of this assumption that H_2O_2 or catalyst may first react with the oxalate ester [12,15].

In recent years, we have studied the chemiluminescence reactions of peroxyoxalate esters, H_2O_2 and several fluorophores in the presence of suitable basic catalysts such as sodium salicylate (SS) and imidazole [19-27]. In this paper, we report a study of PO-CL reaction of diethyl-2-(cyclohexylamino)-5-[(E)-2-phenyl-1-ethenyl]-3,4-furandi-carboxylate (Flu) as a novel fluorescer. The relationship between the chemiluminescence intensity and concentrations of TCPO, sodium salicylate, hydrogen peroxide and fluorescer as well as the influence of temperature on the resulting PO-CL are reported.

Flu
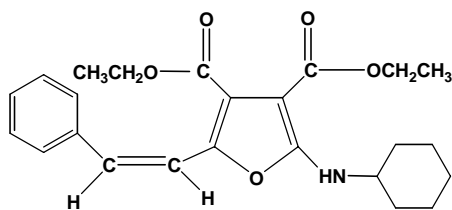
EXPERIMENTAL

Reagents and Solutions

Bis(2,4,6-trichlorophenyl)oxalate (TCPO) was prepared from the reaction of 2,4,6-trichlorophenol with oxalylchloride in the presence of triethylamine as described elsewhere [28]. Hydrogen peroxide (Merck, Perhydrol Suprapur, 30% in water) was assayed by permanganate potassium titration [29] and diluted in ethyl acetate. Diethyl-2-(cyclohexylamino)-5-[(E)-2-phenyl-1-ethenyl]-3,4-furandicarboxylate (Flu) was synthesized in our laboratories, as described before [30]. Reagent grade sodium salicylate (SS, Merck) was used as received. The stock solution of fluorescer (0.005 M) was prepared in a calibrated 50-ml flask by dissolving an appropriate amount of the reagent in ethyl acetate, and protected from light. Stock solutions of sodium salicylate (0.005 M) and the TCPO (0.005 M) in ethyl acetate were prepared shortly before use.

Chemiluminescence Measurements

Chemiluminescence measurements were carried out on a homemade apparatus equipped with a phototube (59 RX Kelman). The instrument was covered with a black sheet, in order to prevent piping of light to the cell. The voltage applied to the phototube was 90 V. The temperature was adjusted to the desired values ± 0.1 °C, using a Thermo Mix Broaun thermostat (Biotechnology Int.). The apparatus was connected to a personal computer *via* a suitable interface (Zag Chem., Tehran, Iran). The experiments were carried out with magnetic stirring (500 rpm) in a light-tight flat-bottom glass cell of 10 mm diameter.

Fluorescence Measurements

Steady-state fluorescence spectra were recorded on a Perkin Elmer, Ls50 spectrofluorimeter instrument. The excitation and emission monochromators were set at 371 and 471 nm, respectively. A spectral bandwidth of 3 nm was used. All experiments were carried out using freshly prepared solutions containing 5×10^{-4}-2.5×10^{-3} M of Flu in an acetonitrile-ethyl acetate (50:50 v/v) solvent mixture, using a 10-mm quartz cuvett.

RESULTS AND DISCUSSION

Peroxyoxalate-chemiluminescence reaction (PO-CL) is one of the most efficient non-biological light producing systems. The mechanism of PO-CL process has been postulated to involve one or more highly energetic intermediate(s) (possibly dioxetane species) capable of exciting a fluorescent receptor molecule [31,32], as shown in the Scheme 1. In preliminary experiments, it was found that the addition of few drops of the stock solution of hydrogen peroxide to an ethyl acetate solution containing TCPO and fluorescer Flu in the presence of suitable catalyst such as SS results in a very intense blue light. The sensitized PO-CL spectrum of Flu together with its fluorescence excitation and emission spectrums is shown in Fig. 1. As it is apparent from Fig. 1, since the light emission steps for both chemiluminescence and fluorescence are essentially analogous, the emission wavelength maxima in both processes are similar (*i.e.*, 471 nm) [19-27,33].

As expected, the intensity of the PO-CL emission was found be affected by the initial concentration of the reactants [20,21,33,]. Thus, in the next steps, the influence of concentrations of Flu, TCPO, H_2O_2, and base catalyst SS, as well the effect of temperature on the PO-CL system was studied. The effects of each of the reagents on the chemiluminescence profile and reaction kinetics were determined under pseudo-first-order condition with hydrogen peroxide in large excess over TCPO. In order to investigate the kinetic profiles of the chemiluminescence process of H_2O_2-TCPO-Flu-SS system from the corresponding CL intensity versus time profiles, a previously reported simplified model was employed [18,33,34]:

$$R \xrightarrow{k_r} X \xrightarrow{k_f} P \tag{5}$$
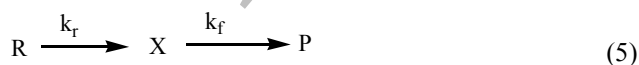
where R, X and P represent pools of reactants, intermediates and products, respectively, and both the reaction steps are irreversible first order reactions. The chemiluminescence signal is proportional to the concentration of intermediate X and the integrated rate equation of CL intensity versus time is:

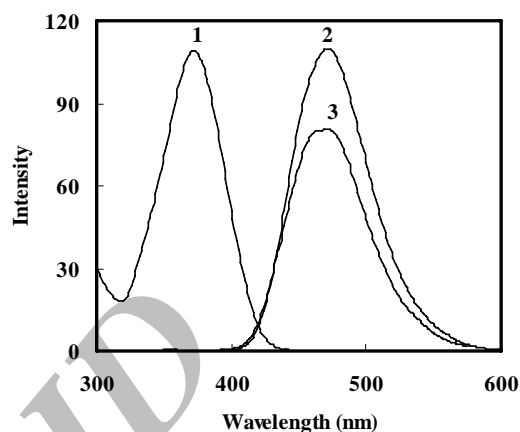$$I_t = [Mk_r/(k_f - k_r)] [\exp(-k_r t) - \exp(-k_f t)] \tag{6}$$

Fig. 1. Fluorescence excitation (1), emission (2) and chemiluminescence (3) spectra of the fluorescer.

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 gives an estimate of the CL intensity at maximum level (J), the time of maximum intensity (T_{max}) and the total yield (Y), as follows:

$$J = M (k_f/k_r)^{[kf/(kr-kf)]} \tag{7}$$

$$T_{max} = [\ln(k_f/k_r)]/[k_f - k_r] \tag{8}$$

$$Y = \int_0^\infty I_t dt = M/k_f \tag{9}$$

In this work, a non-linear least-squares curve fitting program KINFIT [35] 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 other parameters J, T_{max} and Y were then evaluated from Eqs. (7) to (9) using the k_r, k_f and M values. The kinetic parameters thus obtained for all experiments carried out are summarized in Tables 1 and 2.

Figure 3 shows typical response curves (*i.e.*, light intensity versus time) for the PO-CL system of fluorescer Flu (7.5 × 10^{-5} M) in the presence of varying concentrations of TCPO
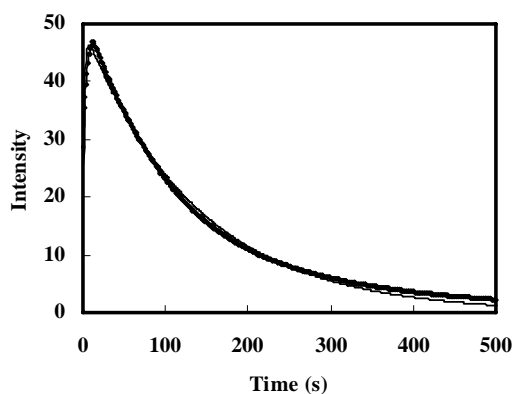
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Fig. 2. Computer fit of the CL intensity-time plot for TCPO-H$_2$O$_2$-Flu-SS system: (♦) experimental point and (-) calculated point

and excess amounts of H$_2$O$_2$. As seen, the peak intensity increases rapidly after mixing and reaches a maximum in less than 35 s, while the decay of light intensity from the maximum occurs at much longer periods o time (*e.g.*, > 14 min at a TCPO concentration upper than 5.0×10^{-4} M). As it obvious from the inset of Fig. 3, there is a nice linear correlation between the chemiluminescence intensity and the TCPO concentration. The basis for such linear correlation has already been discussed in literature [11,36]. 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$_2$O$_2$ is present in large excess [18].

The influence of H$_2$O$_2$ concentration on the PO-CL of fluorescer Flu was studied at constant concentrations of Flu (7.50×10^{-5} M), TCPO (7.50×10^{-4} M) and SS (1.25×10^{-4} M) (Fig. 4). It was found that there is a direct linear relationship between the concentration of hydrogen peroxide and PO-CL intensity of the system, at the concentration ranges of 2.45×10^{-2}-1.84×10^{-1} M. However, further increase in H$_2$O$_2$ concentration (*i.e.*, > 2.45×10^{-1} M) was found to have no significant effect on the PO-CL intensity.

It is interesting to note that, with the excess amount of hydrogen peroxide, the pseudo-first-order fall rate constant, k$_f$, increases linearly with increasing H$_2$O$_2$ concentration with a regression equation k$_f$ = 0.0231[H$_2$O$_2$] + 0.0021 (Table 1) with

a relatively large intercept of about 0.0021 s^{-1}, which is representative of a first-order reaction that is zero-order in concentration of hydrogen peroxide [18,24]. Meanwhile, the pseudo-first-order rate constant for the rise step k$_r$ increased linearly with increasing H$_2$O$_2$ concentration (Table 1). In this case, the linear plot of k$_r$ *vs*. [H$_2$O$_2$] 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 [18]

The PO-CL intensity of a 7.50×10^{-5} M solution of Flu, under the constant concentrations of TCPO (7.50×10^{-4} M) and H$_2$O$_2$ (0.1224 M) was found to increase intensely in the presence of sodium salicylate (SS), most probably due to the catalytic effect of SS on the PO-CL system studied [21,24,37]. In order to investigate the optimal concentration of SS, the CL response of the H$_2$O$_2$-TCPO-Flu system was measured against the varying concentrations of the base catalyat, and the resulting plot is shown in Fig. 5. As seen, the PO-CL intensity rapidly increased with increasing concentration of SS until a concentration of 2.50×10^{-4} M is reached, the observed intensity enhancement being indicative of the catalytic effect of the base. However, further addition of sodium salicylate revealed a gradual decrease in the CL intensity and in total yield, Y (see Table 1). This is most probably due to the quenching effect of the base at higher concentrations, which begins to decompose the reactive intermediate dioxetane and, hence, reduces the PO-CL light [20,21,24].

The effect of Flu concentration, at constant amounts of TCPO, H$_2$O$_2$ and SS was studied and the results are shown in Fig. 6 and Table 1. As it is obvious from Fig. 6, there is a linear increase in CL intensity of the H$_2$O$_2$-TCPO-SS-Flu system with increasing concentration of the fluorescer. In addition, 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 [8,11,12]. Such observations declare the fact that the high-energy cyclic intermediates (*i.e.*, dioxetane species) may transfer energy to a fluorophore *via* the CIEEL mechanism. Previous kinetic works has shown that the charge-transfer steps leading to chemiluminescence are fast relative to the formation of an initial intermediate and, for this reason, the final reactions leading to chemiluminescence are kinetically unobservable [11,15,16,36,37].

Table 1. CL Parameters Evaluated from Computer Fitting of the CL Intensity-Time Plots for H_2O_2-TCPO-Flu-SS System

Parameter changed (M)	Concentration	k_r (s^{-1})	k_f (s^{-1})	M (mV)	J_{exp}	J	T_{exp} (s)	T_{max} (s)	Y (mV s^{-1})
H_2O_2	2.45×10^{-2}	0.056 ± 0.006	0.0023 ± 0.0004	10.86 ± 0.08	9.38	9.47	69	59.1	4681
	6.12×10^{-2}	0.198 ± 0.010	0.0039 ± 0.0005	25.35 ± 0.21	24.51	23.44	23	20.3	6550
	1.22×10^{-1}	0.298 ± 0.016	0.0047 ± 0.0005	38.24 ± 0.28	39.34	35.77	15	14.1	8085
	1.84×10^{-1}	0.401 ± 0.027	0.0067 ± 0.0009	54.96 ± 0.50	58.51	51.25	10	10.4	8166
	2.45×10^{-1}	0.509 ± 0.029	0.0075 ± 0.0011	61.58 ± 0.66	66.93	57.16	10	10	8255
TCPO	2.50×10^{-4}	0.152 ± 0.031	0.0034 ± 0.0005	10.85 ± 0.10	10.58	9.95	32	25.7	3220
	5.00×10^{-4}	0.129 ± 0.009	0.0037 ± 0.0008	19.00 ± 0.25	19.82	17.11	23	28.4	5163
	7.50×10^{-4}	0.184 ± 0.018	0.0047 ± 0.0012	32.16 ± 0.52	35.35	29.22	16	20.5	6857
	1.00×10^{-3}	0.180 ± 0.016	0.0049 ± 0.0011	39.32 ± 0.60	42.54	35.57	16	20.6	8091
	1.50×10^{-3}	0.178 ± 0.007	0.0074 ± 0.0019	39.45 ± 0.92	36.52	34.36	20	18.6	5310
SS	1.25×10^{-5}	0.065 ± 0.004	0.0030 ± 0.0009	18.14 ± 0.29	18.25	15.62	38	49.6	6007
	2.50×10^{-5}	0.124 ± 0.011	0.0047 ± 0.0001	30.67 ± 0.59	33.15	26.96	21	27.3	6512
	7.50×10^{-5}	0.202 ± 0.014	0.0046 ± 0.0008	35.15 ± 0.40	37.68	32.19	15	19.2	7658
	1.25×10^{-4}	0.287 ± 0.014	0.0056 ± 0.0007	41.69 ± 0.37	42.03	38.19	14	15.7	7445
	1.75×10^{-4}	0.302 ± 0.013	0.0062 ± 0.0006	44.11 ± 0.28	44.07	40.64	14	13.1	7069
	2.50×10^{-4}	0.597 ± 0.003	0.0073 ± 0.0007	48.99 ± 0.32	46.86	46.38	12	7.5	6693
	5.00×10^{-4}	0.607 ± 0.015	0.0105 ± 0.0018	59.87 ± 0.71	42.60	55.74	7	6.8	5691
Flu	2.50×10^{-5}	0.163 ± 0.008	0.0051 ± 0.0004	23.54 ± 0.52	20.91	19.89	16	24.9	3482
	5.00×10^{-5}	0.166 ± 0.016	0.0053 ± 0.0001	26.27 ± 0.46	28.64	2345	17	21.4	4957
	1.00×10^{-4}	0.186 ± 0.018	0.0045 ± 0.0001	35.43 ± 0.58	39.40	32.29	16	20.5	7821
	1.50×10^{-4}	0.188 ± 0.027	0.0049 ± 0.0001	46.74 ± 0.79	53.8	43.06	13	16.6	9481
	2.00×10^{-4}	0.169 ± 0.015	0.0042 ± 0.0001	48.31 ± 0.60	54.84	43.94	16	22.4	11421
	2.50×10^{-4}	0.195 ± 0.019	0.0048 ± 0.0001	49.70 ± 0.81	55.99	45.29	14	19.5	10419

Table 2. The CL Parameters Evaluated from Computer Fitting of the CL Intensity-Time Plots for H_2O_2-TCPO-Flu-SS System at Various Temperatures

T (°C)	k_r (s^{-1})	k_f (s^{-1})	M (mV)	J_{exp} (mV)	J (mV)	T_{exp} (s)	T_{max} (s)	Y (mV s^{-1})
20	0.093 ± 0.004	0.0018 ± 0.0003	13.53 ± 0.10	13.86	12.50	33	42.9	7353
30	0.139 ± 0.010	0.0036 ± 0.0008	29.65 ± 0.38	31.5	26.90	21	27.0	8236
40	0.204 ± 0.024	0.0070 ± 0.0006	52.49 ± 1.24	57.02	46.57	14	17.1	7498
50	0.297 ± 0.046	0.0105 ± 0.0009	83.16 ± 2.54	91.83	73.57	10	11.7	7920

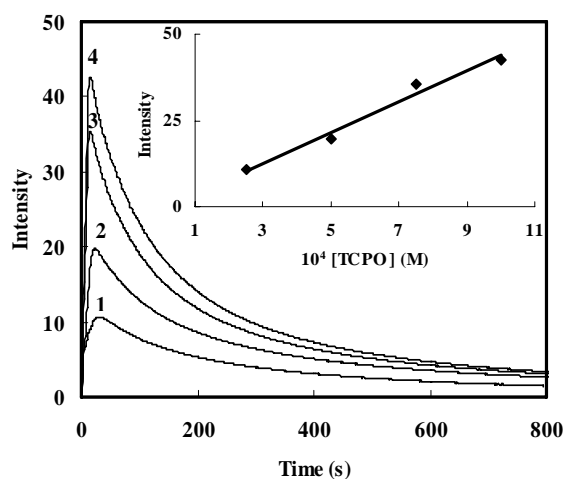**Fig. 3.** Effect of TCPO concentration on the CL intensity of TCPO-H_2O_2-Flu-SS system in ethyl acetate solution: $[H_2O_2] = 1.22 \times 10^{-1}$ M, [SS] = 5.00×10^{-5} M, [Flu] = 7.50×10^{-5} M, TCPO = (1) 2.50×10^{-4} M, (2) 5.00×10^{-4} M, (3) 7.50×10^{-4} M, (4) 1.00×10^{-3} M.
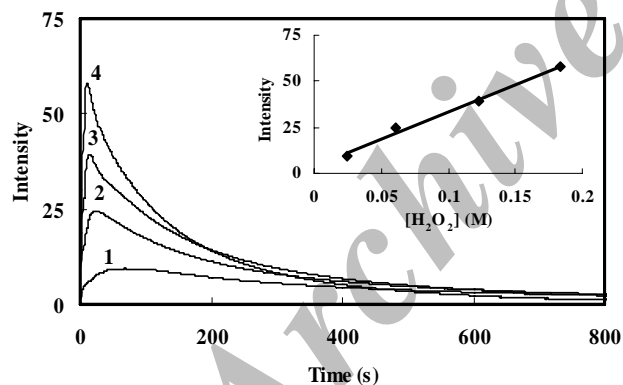
Fig. 4. Effect of H_2O_2 concentration on the CL intensity of TCPO-H_2O_2-Flu-SS system in ethyl acetate solution: [TCPO] = 7.5×10^{-4} M, [Flu] = 7.5×10^{-5} M, [SS] = 1.25×10^{-4}M, $[H_2O_2]$ = (1) 2.45×10^{-2} M, (2) 6.12×10^{-2} M, (3) 1.22×10^{-1} M, (4) 1.84×10^{-1} M.

The influence of solution temperature on the chemiluminescence of the H_2O_2-TCPO-Flu-SS system, at constant concentrations of all reagents involved, was studied and the resulting response curves at 20, 30, 40 and 50 °C are shown in Fig. 7, and the resulting CL parameters for the
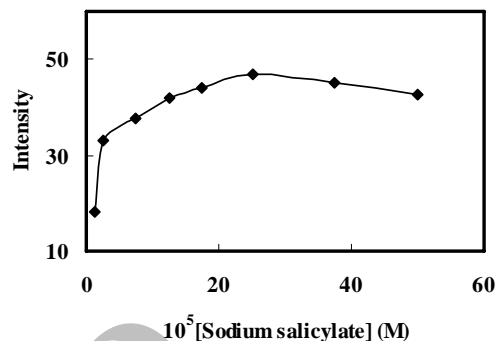

Fig. 5. Effect of SS on the CL intensity of TCPO-H_2O_2-Flu-SS system in ethyl acetate solution: $[H_2O_2] = 1.22 \times 10^{-1}$ M, [TCPO] = 7.5×10^{-4} M, [Flu] = 7.50×10^{-5} M.

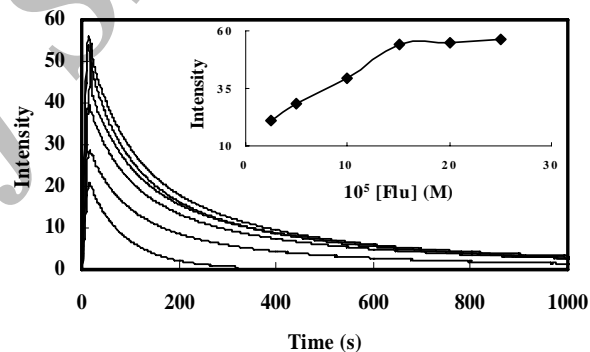**Fig. 6.** Effect of Flu concentration on the CL intensity of TCPO-H_2O_2-Flu-SS system in ethyl acetate solution: $[H_2O_2] = 1.22 \times 10^{-1}$ M, [TCPO] = 7.50×10^{-4} M, [SS] = 5.0×10^{-5} M, [Flu]: (1) 2.50×10^{-5} M, (2) 5.00×10^{5} M, (3) 1.00×10^{-4} M, (4) 1.50×10^{-4} M, (5) 2.00×10^{-4} M, (6) 2.50×10^{-4} M.
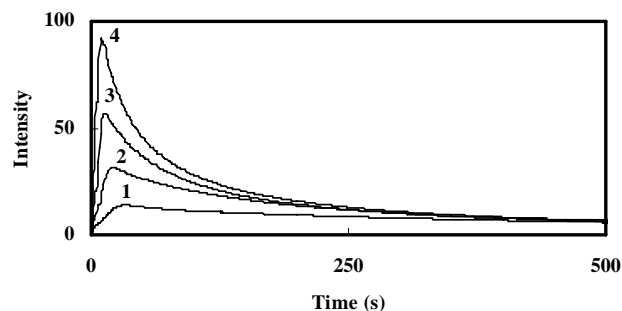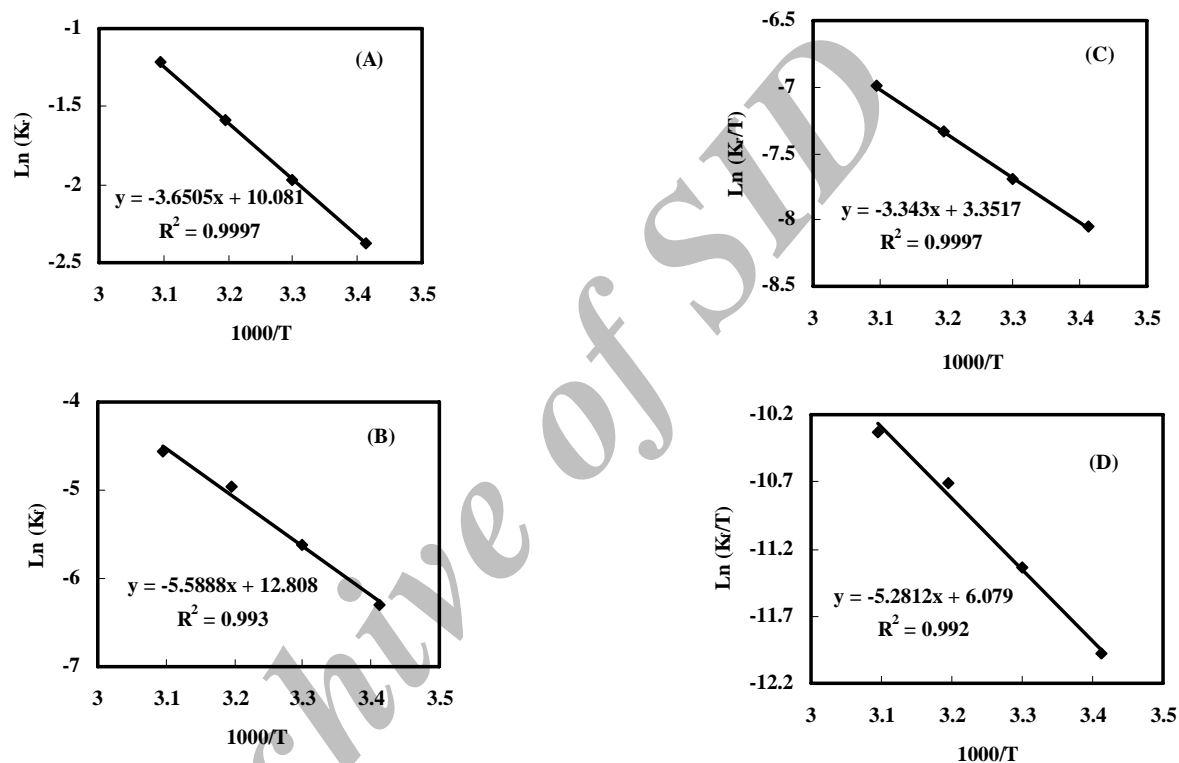

Fig. 7. The CL intensity-time plot for TCPO-H_2O_2-Flu-SS system in ethyl acetate solution at 293 K (1), 303 K (2), 313 K (3) and 323 (K) (4).

Table 3. Activation Parameters of the Rise and Fall Processes for the H_2O_2-TCPO-Flu-SS System

Step	E_a (kJ mol^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	$\Delta G^{\ddagger}_{293K}$ (kJ mol^{-1})
Rise	30.5 ± 2.0	28.1 ± 3.1	-169 ± 2.2	77.6 ± 2.7
Fall	42.1 ± 2.6	39.7 ± 4.0	-160 ± 4.3	86.5 ± 3.9

Fig. 8. Arrhenius plots of $\ln k_r$ *vs.* 1/T (A) and of $\ln k_f$ *vs.* 1/T (B), and Eyring plots of $\ln(k_r/T)$ *vs.* 1/T (C) and of $\ln(k_f/T)$ *vs.* 1/T (D) for TCPO-H_2O_2-Flu-SS system in ethyl acetate solution.

system are summarized in Table 2. As it is illustrated in Fig. 7 and Table 2, the PO-CL intensity increased with increasing temperature, although the total light yield (Y) do not show a systematic change with temperature. This is indicative of o the fact that the higher CL intensities of the PO-CL at higher temperatures are solely due to the rate constants [24].

The activation energies for the rise and fall steps of the PO-CL process were obtained from the slope of the corresponding Arrhenius plots of $\ln k_r$ *vs.* (1/T) (Fig. 8A) and $\ln k_f$ *vs.* 1/T (Fig. 8B) [38], and the resulting E_a^r and E_a^f values are compared in Table 3. The thermodynamic parameters of activation $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated by using Eyring

transition state theory [39], from the slope and intercept of linear plot of $\ln(k/T)$ *vs.* 1/T, respectively, for the rise and fall steps (Fig 8C and 8D). The resulting activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and ΔG are also included in Table 3. The activation parameters thus obtained for both rise and fall steps of the studied PO-CL system are consistent with the discussions and mechanism discussed in the text, and reported before [11-15,18,23,24,31].

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