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A study of chemiluminescence from reaction of bis(2,4,6-trichlorophenyl)oxalate, hydrogen peroxide and an optical brightener 5-(3-anilino-5-chloroanilino)-2-{(*E*)-2-[4-(3-anilino-5-chloroanilino)-2-sulfophenyl]-1-ethenyl}-1-benzenesulfonic acid

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Abstract

The chemiluminescence (CL) arising from reaction of bis(2,4,6-trichlorophenyl)oxalate (TCPO) with hydrogen peroxide in the presence of a brightener 5-(3-anilino-5-chloroanilino)-2-{(*E*)-2-[4-(3-anilino-5-chloroanilino)-2-sulfophenyl]-1-ethenyl}-1-benzenesulfonic acid (Bri) has been studied. The relationship between the chemiluminescence intensity and concentrations of TCPO, sodium salicylate and hydrogen peroxide is reported. The chemiluminescence parameters including intensity at maximum CL, time at maximum intensity, total light yield 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 fall step were evaluated from the temperature dependence of k_f values.

Keywords: Peroxyoxalate-chemiluminescence; Brightener; H_2O_2; TCPO; Activation parameters

1. Introduction

The chemiluminescent systems based upon the reaction between various oxalic acid derivatives and hydrogen peroxide in the presence of a suitable fluorophore was first described by Chandross [1]. Since then, the peroxyoxalate-chemiluminescence (PO-CL) reaction has become one of the most frequently used analytical chemiluminescence schemes [2,3]. PO-CL is based on the reaction of hydrogen peroxide with an activated oxalate, leading to the formation of one or more energy-rich intermediate(s), capable of exciting a large number of fluorophores [4], through the chemically initiated electron exchange luminescence (CIEEL) mechanism [5]. The reaction has dual scopes, by allowing either hydrogen peroxide or the fluorophore to be the limiting component in the reaction. It has consequently been used both for the ultra-trace determination of hydrogen peroxide in flow injection analysis systems and for post-column reaction detection of fluorophores following separation by liquid chromatography [6,7]. The PO-CL as a highly efficient chemiluminescent system enables the excitation of various fluorophores having emission wavelengths from the ultraviolet to near infrared, which facilitates its utilization for numerous analytical applications [8–11].

Fluorescent brighteners are in increased use as functional pigments in the process of chemical bleaching to the fibers, papers and pulps in order to make them appear brighter. They increase the whiteness by a process of absorption of light in ultraviolet region (330–380 nm) and emission of a visible

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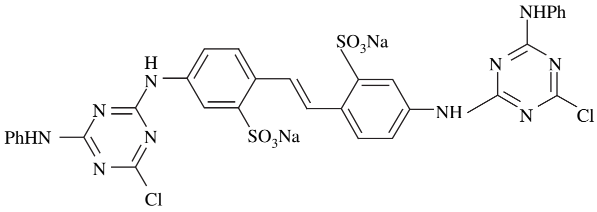
blue light (400–450 nm) [12–15]. Optical brighteners have been used for many years to improve the color of various plastics, by making inherent yellowness in discolored polymers or by imparting unique, robust color to specially plastic products [16].

Various disodium 4,4′-bis(1,3,5-triazin-6-yl)diaminostilbene-2,2′-disulfonate derivatives, which were symmetrically substituted on both triazine moieties, were used as fluorescent brighteners for wool and cotton [17,18]. Since optical brighteners fluoresce under exposure to an ultraviolet lamp or black light, they are usually used as very sensitive tracers. It is thus necessary for the fluorescent brighteners to possess a high fluorescence activity as well as a high quality of whiteness and fastness [19]. Several analytical and clinical applications of optical brightener have also been reported [20–22].

In this paper, we report the first study of peroxyoxalate-chemiluminescence from the reaction of 5-(3-anilino-5-chloroanilino)-2-{(*E*)-2-[4-(3-anilino-5-chloroanilino)-2-sulfophenyl]-1-ethenyl}-1-benzenesulfonicacid, Bri, as an efficient fluorescence brightener.



Bri

2. Experimental

2.1. 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 [23]. TCPO was synthesized as described by Mohan [23]. Hydrogen peroxide (Merck; Perhydrol Suprapur, 30% in water) was assayed by permanganate potassium titration [24]. The brightener Bri was synthesized and purified in our laboratories as reported elsewhere [25]. The stock solution of brightener (10 mM) was prepared in a calibrated 50-ml flask by dissolving an appropriate amount of Bri in smallest volume of methanol and diluted to the mark with acetonitrile–ethylacetate (1:1 v/v) mixture and protected from light. Stock solutions of sodium salicylate (0.01 M in MeOH) and the TCPO (10 mM in acetonitrile–ethylacetate 50:50 v/v) were prepared shortly before use.

2.2. 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 and the temperature was set at 25 °C. The apparatus was connected to a personal computer via a suitable interface (Zag Chem, Tehran, Iran).

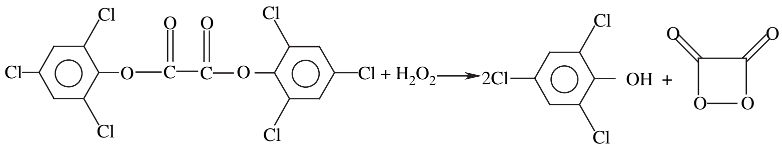
Experiments were carried out with magnetic stirring (500 rpm) in a light-tight flat-bottom glass cell of 10 mm diameter. The temperature was adjusted to the desired values ± 0.1 °C, using a Thermo Mix Broaun thermostat (Biotechnology Int.)

2.3. Fluorescence measurements

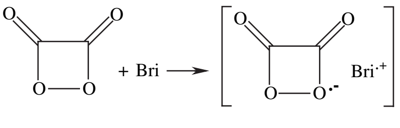
Steady-state fluorescence spectra were recorded on a Perkin Elmer, L50 spectrofluorimeter instrument. The excitation and emission monochromators were set at 390 and 440 nm, respectively. A spectral bandwidth of 3 nm was used. All experiments were carried out using freshly prepared solutions containing 4.5×10^{-5} M of brightener in the mixed acetonitrile–ethylacetate (50:50 v/v) solvent, using a 10-mm quartz cuvette.

3. 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 at least one highly energetic intermediate (possibly a dioxetane species) capable of exciting a fluorescent receptor molecule [26,27], as shown in the following scheme:



(1)



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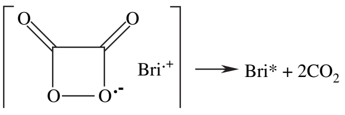

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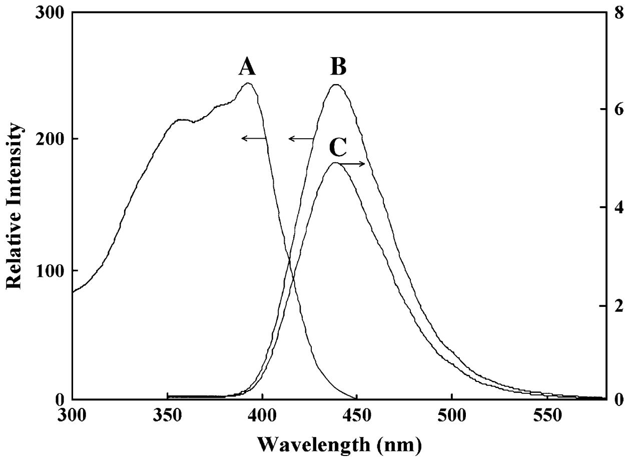

Fig. 1. Fluorescence excitation (A), emission (B) and chemiluminescence (C) spectra of Bri.

$$Bri^{*} \xrightarrow{k_1} Bri + h\nu \tag{4}$$

$$Bri^{*} \xrightarrow{k_{nr}} Bri + heat \tag{5}$$

In preliminary experiments, it was found that the addition of excess amount of hydrogen peroxide to a nearly colorless acetonitrile–ethylacetate (1:1 v/v) solution containing 5.0×10^{-4} M of brightener and 0.01 M TCPO results in an intense blue light. The chemiluminescence spectrum for TCPO–H_2O_2 reaction containing the fluorescer Bri was recorded and compared with the fluorescence spectrum of the fluorescer, recorded under comparable experimental conditions (Fig. 1). As is obvious from Fig. 1, good correspondence was obtained for the PO-CL and fluorescence spectral distributions of brightener B, demonstrating that the singlet excited state of the fluorescent additive is formed in the reaction and is the emitting species [28,29].

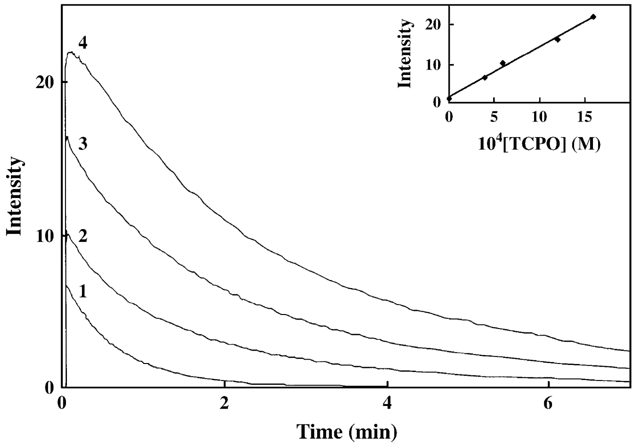

Fig. 2. CL intensity as a function of time for reaction of H_2O_2 (0.34 M), sodium salicylate (2.0×10^{-4} M) and Bri (4.0×10^{-4} M) in acetonitrile–ethylacetate (1:1 v/v) mixture in the presence of varying concentrations of TCPO: (1) 4.0×10^{-4} M, (2) 6.0×10^{-4} M, (3) 1.2×10^{-3} M, (4) 1.6×10^{-3} M.

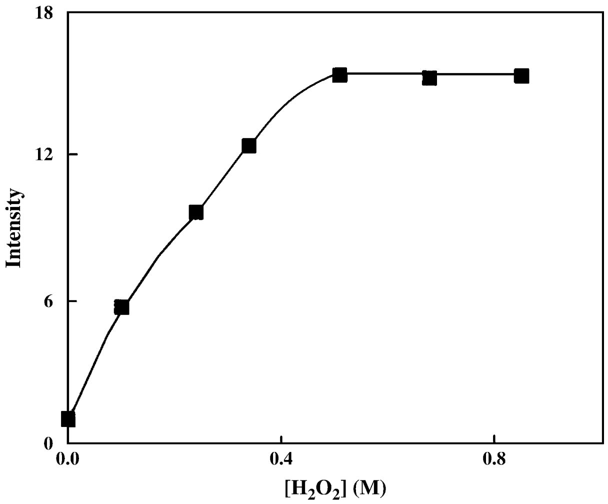

Fig. 3. Effect of H_2O_2 concentration on the CL intensity of TCPO–H_2O_2–Bri system.

Fig. 2 shows typical response curves (i.e., light-intensity versus time) for the PO-CL system of brightener Bri (4.0×10^{-4} M) in the presence of varying concentrations of TCPO. As seen, the peak intensity increases rapidly after mixing and reaches a maximum in a few seconds. Whereas, the decay of light-intensity from the maximum occurs at much longer periods (e.g., >7 min at a TCPO concentration of 1.6×10^{-4} M). As it obvious from the inset of Fig. 2, 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 [30].

The influence of H_2O_2 concentration on the PO-CL of brightener Bri was studied at constant concentrations of Bri (4.0×10^{-4} M) and TCPO (1.2×10^{-3} M) (Fig. 3). 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 studied (i.e., 0.1–0.5 M). It is noteworthy that further increase in H_2O_2 concentration was found to have no measurable effect on the PO-CL intensity.

The PO-CL intensity of a 4.0×10^{-4} M solution of Bri, under the optimal constant concentrations of TCPO and H_2O_2 was found to increase significantly in the presence of sodium salicylate, a behavior that is clearly indicative of the catalytic effect of the salt on the PO-CL system studied [31].

In order to investigate the optimal concentration of sodium salicylate, the CL response of the H_2O_2–TCPO–Bri system was measured against the varying concentrations of the base and the resulting plot is shown in Fig. 4. The PO-CL intensity sharply increased with increasing concentration of sodium salicylate until a concentration of 5.6×10^{-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. This is most probably due to the quenching effect of the base at higher concentrations, which begins to decompose the reactive intermediate, dioxetane dione, and hence reduces the PO-CL light [32].

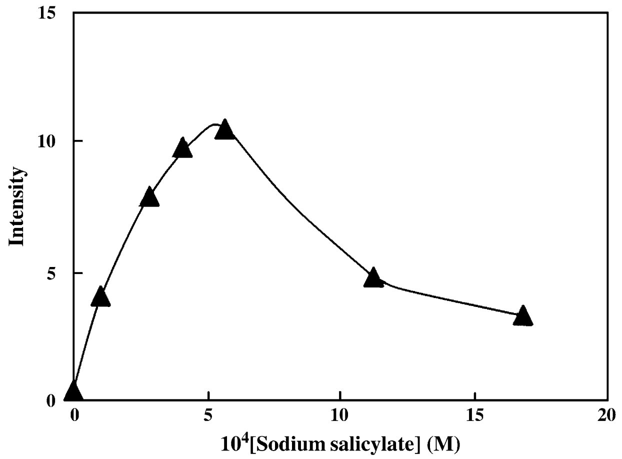

Fig. 4. Effect of sodium salicylate on the CL intensity of TCPO–H_2O_2–Bri system.

The influence of solution temperature on the chemiluminescence of the H_2O_2–TCPO–Bri 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. 5. As it is illustrated in Fig. 5, the PO-CL intensity increased with increasing temperature, due to the enhanced population of the activated Bri* molecules at higher temperatures. While, the decay of light-intensity from the maximum occurs at shorter times, as the solution temperature increases.

In order to investigate the kinetic profiles of the chemiluminescence process of H_2O_2–TCPO–Bri system from the corresponding CL intensity versus time profiles, a previously reported simplified model was employed [30,33,34]:

$$R \xrightarrow{k_r} X \xrightarrow{k_f} P \qquad (6)$$

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:

$$I_t = \left[Mk_r/\left(k_f - k_r\right)\right]\left[\exp(-k_r t) - \exp\left(-k_f t\right)\right] \qquad (7)$$

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, respectively, the first order rate constants for the rise and fall of the burst of CL. 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 yield (Y), as follows:

$$J = M\left(k_f/k_r\right)^{\left[k_f/\left(k_r - k_f\right)\right]} \qquad (8)$$

$$T_{\max} = \left[\ln\left(k_f/k_r\right)\right]/\left[k_f - k_r\right] \qquad (9)$$

$$Y = \int_0^\infty I_t \mathrm{d}t = M/k_f \qquad (10)$$

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. 6. The other parameters J, $T_{\max}$ and Y were then evaluated from Eqs. (8)–(10) 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. The data given in Table 1 indicate that there is a satisfactory agreement between the calculated (J) and experimental ($J_{\exp}$) values of the intensity at maximum CL.

The activation energy for the fall step of the PO-CL process was obtained from the slope of the corresponding Arrhenius plot of $\ln k_f$ versus $1/T$ (Fig. 7A) and the activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were calculated by using Eyring transition-state theory [36], from the slope and intercept of the linear

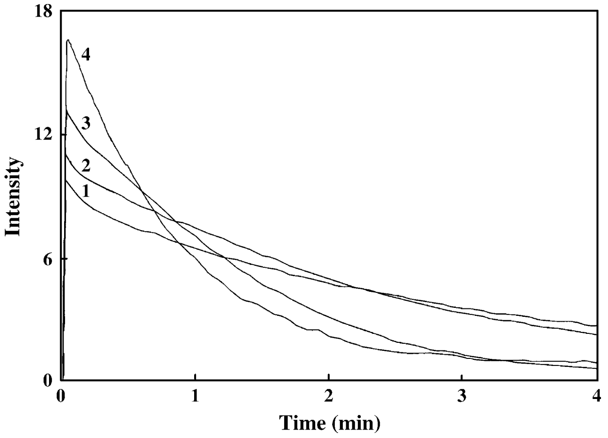

Fig. 5. The CL intensity–time plot for TCPO–H_2O_2–Bri system at 293 K (1), 303 K (2), 313 K (3) and 323 K (4). Experimental conditions: Bri, 4.0×10^{-4} M; TCPO, 1.2×10^{-3} M; H_2O_2, 0.4 M; sodium salicylate, 5.0×10^{-4} M.

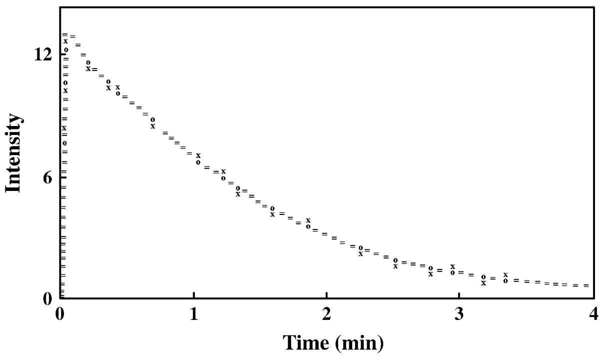

Fig. 6. Computer fit of the CL intensity–time plot for TCPO–H_2O_2–Bri system at 303 K (Fig. 5): (×) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plot.

Table 1
The CL parameters evaluated from computer fitting of the CL intensity–time plots for H_2O_2–TCPO–Bri system

Parameter changed	Concentration (M)	k_r (min^{-1})	k_f (min^{-1})	M (μV)	J_{exp}	J	T_{exp} (min)	T_{max} (min)	Y (μV/min)
H_2O_2	0.102	29.7 ± 1.6	0.36 ± 0.08	8.5 ± 0.12	7.9	9	0.16	0.142	21.77
	0.238	98.2 ± 3.4	0.44 ± 0.06	9.6 ± 0.10	9.5	10	0.06	0.057	26.13
	0.340	103.2 ± 4.3	0.54 ± 0.01	11.3 ± 0.10	11.2	11	0.048	0.051	20.84
	0.510	78.3 ± 3.4	0.76 ± 0.02	15.6 ± 0.27	15.3	15	0.033	0.058	20.46
TCPO	4.0×10^{-4}	51.7 ± 4.6	1.52 ± 0.01	6.92 ± 0.06	6.7	7	0.012	0.023	4.54
	6.0×10^{-4}	96.5 ± 4.3	0.67 ± 0.01	10.2 ± 0.2	10.2	10	0.024	0.031	15.81
	12.0×10^{-4}	132.3 ± 4.7	0.47 ± 0.08	16.35 ± 0.15	16.3	16	0.035	0.044	34.46
	16.0×10^{-4}	72.8 ± 3.1	0.35 ± 0.008	22.8 ± 0.27	21.9	22	0.071	0.072	64.11
Sodium salicylate	8.0×10^{-5}	23.1 ± 0.67	0.21 ± 0.004	5.95 ± 0.05	5.6	6	0.23	0.21	27.96
	2.8×10^{-4}	81.7 ± 3.0	0.40 ± 0.009	8.12 ± 0.08	7.9	8	0.05	0.06	20.16
	4.0×10^{-4}	86.4 ± 3.9	0.60 ± 0.01	9.85 ± 0.14	10.1	10	0.03	0.05	16.38
	5.6×10^{-4}	138.0 ± 5.3	1.10 ± 0.01	10.1 ± 0.11	10.2	10	0.02	0.03	9.30
	1.12×10^{-3}	183.3 ± 7.1	1.84 ± 0.04	4.97 ± 0.05	4.9	5	0.01	0.02	2.70
	1.68×10^{-3}	187.1 ± 5.4	2.4 ± 0.08	3.72 ± 0.07	3.4	3	0.01	0.03	1.51

Table 2
The CL parameters evaluated from computer fitting of the CL intensity–time plots for H_2O_2–TCPO–Bri system at various temperatures

T(K)	k_r (min^{-1})	k_f (min^{-1})	M (μV)	I (μV)	J (μV)	T (min)	T_{max} (min)	$T_{1/2}$ (min)	$T_{3/4}$ (min)	Y (μV/min)
293	82.1 ± 2.4	0.35 ± 0.004	9.5 ± 0.08	10.1	9	0.04	0.06	1.7	0.50	17.05
303	48.2 ± 1.7	0.43 ± 0.008	11.3 ± 0.12	11.5	11	0.06	0.09	1.6	0.60	26.10
313	52.8 ± 2.9	0.77 ± 0.002	13.8 ± 0.12	13.4	13	0.05	0.08	1.1	0.50	17.95
323	32.2 ± 1.1	1.13 ± 0.02	17.5 ± 0.15	16.3	16	0.06	0.08	0.9	0.40	15.46

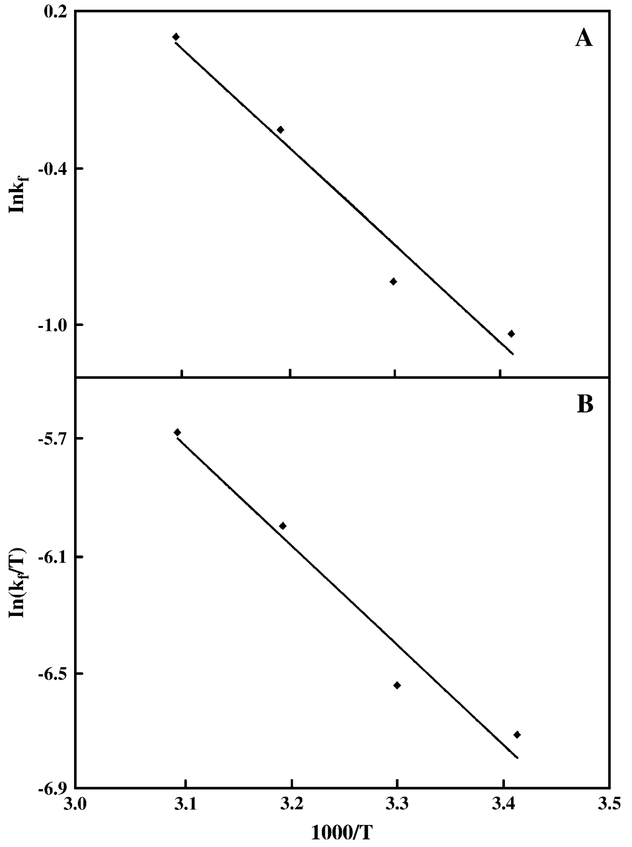

Fig. 7. Arrhenius (A) and Eyring (B) plots for TCPO–H_2O_2–Bri system.

plot of $\ln(k_f/T)$ versus $1/T$, respectively. The resulting activation parameters thus determined for the fall of the PO-CL burst are as follows: $E_a = 31.4 \pm 4.2\ \text{kJ mol}^{-1}$, $\Delta H^{\ddagger} = 28.9 \pm 4.1\ \text{kJ mol}^{-1}$, $\Delta S^{\ddagger} = 42 \pm 13\ \text{J mol}^{-1}\ \text{K}^{-1}$ and $\Delta G^{\ddagger} = 8.27 \pm 0.12\ \text{kJ mol}^{-1}$.

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