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# Evaluation and determination of kinetic and thermodynamic chemiluminescence characteristics of a novel peroxyoxalate system using two new triazine derivative

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**Abstract**

The chemiluminescence arising from the reaction of bis(2,4,6-trichlorophenyl)oxalate (TCPO) with hydrogen peroxide in the presence of fluorescent brighteners 4,4'-Bis{[4-anilino-6-bis(2-hydroxyethyl)amino-1,3,5-triazin-2-yl]amino} stilbene-2,2'-disulfonic acid- disodium salts (Triaz I), 4,4'-Bis{[4-6-anilino -1,3,5-triazin-2-yl]amino}stilbene-2,2'-disulfonic acid- disodium salts  (Triaz II) has been studied. The influence of concentration of Triazinyl, TCPO, hydrogen peroxide, catalysts concentration, catalyst type and temperature on the chemiluminescence was investigated. The kinetic parameters for the peroxyoxalate-chemiluminescence of Triazinyl were appraise from computer fitting of the resulting intensity–time plots. The activation parameters such as $E_a$ and G, were evaluated from temperature dependence of the corresponding fall rate constants.

## 1. Introduction

The peroxyoxalate-hydrogen peroxide system is the only chemiluminescent reaction supposed to involve a molecular chemically initiated electron exchange luminescence (CIEEL) mechanism with proven high quantum yields [1] . This system consists of a base-catalyzed reaction of activated oxalic phenyl esters with hydrogen peroxide in the presence of highly fluorescent aromatic hydrocarbons with low oxidation potentials as chemiluminescent activators. Mechanistic studies using various oxalic esters and a variety of experimental conditions led to the determination of rate constants for several reaction steps as well as the proposal of different high-energy intermediate structures [2-4]. The increasing interest in the peroxyoxalate-chemiluminescence (PO-CL) system is due to its high ability for the detection of quenchers and analytical applicability as a sensitive tool for studying and quantifying numerous analytes [5-9].

Fluorescent brighteners are increased use as functional pigments in the process of chemical bleaching of the fiber, paper and pulp in order to make them appear brighter. They increase the whiteness by a process of absorption of the light in the ultraviolet region (330-380 nm) and the emission of the visible blue light (400-450 nm) [10, 11]. Optical brighteners have been used for many years to improve the color of various plastics, by making inherent yellowness in discolored polymers or by importing unique, robust color to especially plastic products [12].

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It has already been reported that the substitution of strong electron-donating or electron-attracting substituents on imidazole molecule or replacement of its pyrrole nitrogen by sulfur will result in the loss of catalytic activity of imidazole derivatives [5, 13, 14].

Various disodium salt derivatives of 4, 4'- bis (1, 3, 5-triazin-6-yl) diaminostilbene-2, 2'-disulfonate, which are symmetrically substituted on both triazine moieties, have been used as fluorescent brighteners [15]. Since optical brighteners fluoresce under exposure of ultraviolet lamp or black light, they are usually used as very sensitive tracers. It is thus necessary for the fluorescent brighteners to pass a high fluorescence activity as well as a high quality of whiteness and fastness [16]. Several analytical and clinical applications of optical brightener have also been reported [17].

In this paper, we report the first study of chemiluminescence from reaction of bis-(2,4,6-trchlorophenyl)oxalate (TCPO) and hydrogen peroxide with 4,4'- bis{[4-anilino-6-bis(2-hydroxyethyl)amino-1,3,5-triazazin-2-yl]amino} stilbene-2,2'-disulfonic - disodium salts (Triaz I ) and 4,4'- bis{[4-6-anilino -1,3,5-Triazin-2-yl]amino}stilbene-2,2'-disulfonic - disodium salts (Triaz II) as efficient fluorescence brighteners, in the presence of sodium salicylate, imidazole and 4-methylimidazole as catalysts (Scheme 1). In addition, The activation parameters such as $E_a$ and G, were evaluated from temperature dependence of the corresponding fall rate constants.

## 2. Experimental

### 2.1. Apparatus

Perkin-Elmer LS 50 spectrofluorimeter was used for recording fluorescence and chemiluminescence spectram. Excitation wavelength (SBW=5.0 nm) was 380 nm and emission of chemiluminescence and fluorescence from Triaz (I and II) were 435 and 437 nm. Emissions SBW were 5 and 2.5 nm respectively for chemiluminescence and fluorescence. A Thermomix Broaun model (Biotechnology Ind.) was used for temperature setting. The system was equipped with a stirrer that allowed the mixture of reagents to stir at low speeds.

### 2.2. Chemicals and solutions

TCPO was synthesized as described by Mohan [6]. The reaction was carried out in ethyl acetate (p.a., Merck) imidazole (98%, Merck), 4-methylimidazole (98%, Aldrich), sodium salicylate (Aldrich) were used without further purification. Hydrogen peroxide (Perhydrol Suprapur, 30% in water, Merck) was assayed by the standard potassium permanganate solution. Hydrogen peroxide (30%) was concentrated via freeze drying (using a model FD-1 Eyela freeze dryer, Tokyo, Japan) up to 60% mixed with dimethyl phthalate, in a 1:1 v/v portions, and shake well in an electrical

shaker. After 10 h, the organic phase was separated, dried with anhydrous $Na_2SO_4$ and the $H_2O_2$ concentration was determined by a standard potassium permanganate solution. A stock solution of hydrogen peroxide is 3.2 M. Triazinyl I and II were synthesized and purified in laboratories of the research group of organic chemistry in Mazandaran University. The method used for the synthesis of flurophore triazinyl involved a simplified work-up for the preparation of 4-nitro-toluene-2-sulfonic acid by the use of diethylene glycol instead of water in the preparation of 4, 4'-dinitrostilbene-2, 2'-disulfonic acid [18]. The stock solution of brightener (0.001M) was prepared in basic methanol and protected from light. Stock solutions of sodium salicylate, imidazole and 4-methylimidazole (0.1 M in MeOH) and the TCPO (0.01 M in ethyl acetate) were prepared shortly before use.

### 2.3. Fluorescence measurements

Fluorescence spectra were obtained using a Perkin Elmer-LS 50 series instrument. The excitation monochromator was set at 380 nm with a spectral bandwidth (SBW) of 5.0 nm and the emission spectrum of the brightener was evaluated (SBW 2.5 nm). Experiment was carried out using freshly prepared solutions containing triazinyl ($10^{-5}$ M) in methanol, contained in a 1-cm quartz cuvette.

### 2.4. Chemiluminescence measurements

Chemiluminescence measurements were carried out on a Perkins Elmer-Ls50 spectrofluorimeter by changed to chemiluminescence mode. All reagents solutions were prepared freshly. The temperature was set at 20.0, 30.0, and 40.0°C. Solution A was made with 1.0 ml of TCPO (0.01 M) and 0.5 ml of triazinyl (0.001M) in ethyl acetate and 1.75 ml of ethyl acetate. Solution B contained 2 ml of 3.2 mM hydrogen peroxide and the 1.0 ml of catalyst (0.1 M) in methanol. Solution A was transferred into the instrument quartz cuvette via polypropene syringes. Then 0.1 ml of the B stock solution was injected in the quartz cuvette and the chemiluminescence spectrum was recorded. Final concentrations of reagents are presented at any case of experiments in Table 1-2. The maximum wavelength emission of chemiluminescence and fluorescence from Triaz ( I and II) were 435 and 437 nm respectively. Triaz I and II that have different phenyl branches, the dimension and electronic distribution of molecules are different (Fig.1). This has led to the few differences of maximum emission wavelength and Intensity of fluorescence between Triaz I and II.

## 3. Results and discussion

This work is the first attempt to introduce two new triazine dye derivative as luminophor for peroxyoxalate chemiluminescence system. Peroxyoxalate chemiluminescence (PO-CL) reaction mechanism, kinetic model and application to introduce for new luminophor were described previously. In preliminary experiments, it was found

that the addition of a few drops of the stock solution of hydrogen peroxide to an ethyl acetate solution containing TCPO and triazinyl results an intense blue light. The PO-CL spectrum of triazinyl together with its fluorescence spectrum is shown in Fig. 2. As it is seen, since the light emission steps for both chemiluminescence and fluorescence are necessary analogous, the emission wavelength maxima in both processes for Triaz I and II are similar in some cases (i.e., 433 nm).

As expected, the intensity of the PO-CL emission found to be affected by the initial

concentration of the reactants. Thus, in the next steps, the influence of concentrations of triazinyl, TCPO, $H_2O_2$, and catalysts, as well as the effect of temperature on the PO-CL system was studied and some of the resulting CL data were described.

Table 1.  CL parameters evaluated from computer fitting of the CL intensity-time plots for $H_2O_2$-TCPO-Triazinyl (I) -Sodium salicylate system

| Parameter changed | Consentration | $k_r$ (min $^{-1}$) | $k_f$ (min $^{-1}$) | M (μ V) | I (μ V) | J (μ V) | T (min) | $\tau_{max}$ (min) | Y(μ V. min) |
|---|---|---|---|---|---|---|---|---|---|
| Triaz (I)[a] | $8.06 \times 10^{-4}$ | $75.8 \pm 3.74$ | $0.80 \pm 0.02$ | $39.4 \pm 0.44$ | 40.5 | 38 | 0.050 | 0.060 | 49.3 |
| | $16.1 \times 10^{-4}$ | $69.0 \pm 4.25$ | $1.05 \pm 0.05$ | $62.2 \pm 1.04$ | 64.0 | 58 | 0.035 | 0.061 | 58.9 |
| | $32.2 \times 10^{-4}$ | $74.1 \pm 6.97$ | $3.53 \pm 0.30$ | $44.9 \pm 1.47$ | 47.7 | 39 | 0.035 | 0.043 | 12.7 |
| | $48.3 \times 10^{-4}$ | $67.5 \pm 4.04$ | $7.62 \pm 0.24$ | $45.8 \pm 1.11$ | 46.4 | 35 | 0.035 | 0.037 | 6.4 |
| | $64.5 \times 10^{-4}$ | $58.3 \pm 3.82$ | $13.61 \pm 0.63$ | $51.1 \pm 1.82$ | 43.6 | 33 | 0.025 | 0.032 | 3.7 |
| TCPO [b] | $8.06 \times 10^{-4}$ | $32.6 \pm 7.72$ | $27.64 \pm 5.71$ | $17.4 \pm 4.11$ | 7.8 | 6 | 0.035 | 0.030 | 0.53 |
| | $16.1 \times 10^{-4}$ | $52.6 \pm 5.03$ | $3.54 \pm 0.21$ | $13.1 \pm 0.51$ | 15.7 | 11 | 0.045 | 0.055 | 3.7 |
| | $32.3 \times 10^{-4}$ | $79.3 \pm 3.66$ | $0.87 \pm 0.01$ | $54.8 \pm 0.59$ | 56.7 | 52 | 0.050 | 0.057 | 62.4 |
| | $48.4 \times 10^{-4}$ | $56.7 \pm 2.79$ | $0.54 \pm 0.01$ | $64.0 \pm 0.84$ | 65.8 | 62 | 0.055 | 0.082 | 116.7 |
| | $64.5 \times 10^{-4}$ | $37.2 \pm 1.67$ | $0.46 \pm 0.01$ | $123.9 \pm 1.69$ | 115.2 | 117 | 0.035 | 0.119 | 268.3 |
| $H_2O_2$[c] | $8.33 \times 10^{-3}$ | $73.0 \pm 4.01$ | $0.37 \pm 0.01$ | $25.7 \pm 0.24$ | 26.9 | 25 | 0.045 | 0.072 | 69.0 |
| | $16.6 \times 10^{-3}$ | $72.1 \pm 4.19$ | $0.39 \pm 0.009$ | $48.8 \pm 0.62$ | 52.0 | 47 | 0.055 | 0.072 | 122.3 |
| | $33.3 \times 10^{-3}$ | $48.8 \pm 2.79$ | $0.46 \pm 0.01$ | $65.5 \pm 1.06$ | 69.8 | 63 | 0.065 | 0.096 | 152.1 |
| | $50 \times 10^{-3}$ | $48.0 \pm 3.4$ | $0.45 \pm 0.01$ | $90.8 \pm 1.38$ | 98.5 | 88 | 0.040 | 0.081 | 198.9 |
| | $66.6 \times 10^{-3}$ | $46.3 \pm 2.71$ | $0.50 \pm 0.02$ | $114.1 \pm 1.59$ | 126.3 | 109 | 0.065 | 0.098 | 224.8 |
| | $83.3 \times 10^{-3}$ | $46.4 \pm 3.00$ | $0.60 \pm 0.02$ | $122.7 \pm 2.4$ | 140.0 | 126 | 0.045 | 0.094 | 203.9 |
| Sodium salicylate[d] | 0.00 | $12.6 \pm 0.22$ | $0.12 \pm 0.001$ | $11.8 \pm 0.06$ | 11.2 | 11 | 0.385 | 0.37 | 96.9 |
| | $8.06 \times 10^{-4}$ | $15.7 \pm 0.26$ | $0.12 \pm 0.001$ | $32.3 \pm 0.14$ | 30.2 | 31 | 0.175 | 0.30 | 253.5 |
| | $16.1 \times 10^{-4}$ | $50.9 \pm 1.76$ | $0.18 \pm 0.02$ | $52.8 \pm 0.30$ | 50.8 | 52 | 0.070 | 0.11 | 288.1 |
| | $32.3 \times 10^{-4}$ | $41.4 \pm 2.34$ | $0.70 \pm 0.03$ | $148.6 \pm 2.1$ | 171.8 | 142 | 0.06 | 0.10 | 211.2 |
| | $48.4 \times 10^{-4}$ | $51.4 \pm 2.18$ | $0.44 \pm 0.007$ | $70.9 \pm 0.50$ | 70.3 | 68 | 0.035 | 0.09 | 168.9 |
| | $64.5 \times 10^{-4}$ | $47.1 \pm 2.14$ | $0.51 \pm 0.02$ | $68.8 \pm 0.73$ | 68.9 | 67 | 0.04 | 0.09 | 134.8 |

Constant reagent concentrations:
[a] $[H_2O_2]$=0.051, [sod]=$1.6 \times 10^{-3}$, [TCPO]=$3.2 \times 10^{-3}$ - [b] $[H_2O_2]$=0.051, [sod]=$1.6 \times 10^{-3}$, [Triaz I]= $1.6 \times 10^{-4}$

[c] [Triaz I]= $1.6 \times 10^{-4}$, [sod]= $6.4 \times 10^{-4}$, [TCPO]=$6.4 \times 10^{-3}$ - [d] $[H_2O_2]$=0.051, [Triaz I]= $1.6 \times 10^{-4}$, [TCPO]=$6.4 \times 10^{-3}$

Table 2: CL parameters evaluated from computer fitting of the CL intensity-time plots for $H_2O_2$-TCPO-Triazinyl (II) -Sodium salicylate system

| Parameter changed | Consentration | $k_r$ (min$^{-1}$) | $k_f$ (min$^{-1}$) | M ($\mu$ V) | I ($\mu$ V) | J ($\mu$ V) | T (min) | $\tau_{max}$ (min) | Y ($\mu$ V. min) |
|---|---|---|---|---|---|---|---|---|---|
| TCPO[a] | $8.06 \times 10^{-4}$ | $13.3 \pm 1.8$ | $11.5 \pm 1.6$ | $8.4 \pm 1.8$ | 8 | 6 | 0.07 | 0.07 | 3.15 |
| | $16.1 \times 10^{-4}$ | $29.6 \pm 3.4$ | $3.7 \pm 0.41$ | $28.3 \pm 5.0$ | 28 | 28 | 0.05 | 0.07 | 21.7 |
| | $32.2 \times 10^{-4}$ | $36.0 \pm 2.7$ | $0.88 \pm 0.03$ | $87.7 \pm 3.9$ | 82 | 86 | 0.06 | 0.10 | 160.5 |
| | $48.3 \times 10^{-4}$ | $40.1 \pm 2.8$ | $0.47 \pm 0.02$ | $126.1 \pm 4.3$ | 120 | 128 | 0.07 | 0.11 | 373.5 |
| | $64.5 \times 10^{-4}$ | $29.4 \pm 1.4$ | $0.43 \pm 0.01$ | $146.3 \pm 4.5$ | 140 | 148 | 0.08 | 0.14 | 686.9 |
| Triaz (II)[b] | $8.06 \times 10^{-4}$ | $27.1 \pm 2.3$ | $0.74 \pm 0.04$ | $35.2 \pm 2.9$ | 33 | 32 | 0.07 | 0.12 | 107.1 |
| | $16.1 \times 10^{-4}$ | $28.4 \pm 2.6$ | $1.22 \pm 0.09$ | $99.5 \pm 7.1$ | 97 | 97 | 0.08 | 0.11 | 147.7 |
| | $32.3 \times 10^{-4}$ | $34.2 \pm 2.9$ | $2.21 \pm 0.14$ | $102.2 \pm 6.9$ | 126 | 112 | 0.07 | 0.085 | 91.1 |
| | $48.4 \times 10^{-4}$ | $39.5 \pm 3.4$ | $4.8 \pm 0.33$ | $146.4 \pm 10.3$ | 140 | 144 | 0.05 | 0.06 | 53.5 |
| | $64.5 \times 10^{-4}$ | $40.7 \pm 4.7$ | $11.4 \pm 1.2$ | $73.1 \pm 16.1$ | 78 | 76 | 0.03 | 0.04 | 19.4 |
| $H_2O_2$[c] | $8.33 \times 10^{-3}$ | $2.42 \pm 0.08$ | $0.90 \pm 0.03$ | $19.7 \pm 0.5$ | 14 | 17 | 0.70 | 0.65 | 21.93 |
| | $16.6 \times 10^{-3}$ | $3.37 \pm 0.10$ | $0.44 \pm 0.006$ | $31.5 \pm 0.23$ | 29 | 26 | 0.45 | 0.50 | 70.63 |
| | $33.3 \times 10^{-3}$ | $3.50 \pm 0.10$ | $0.48 \pm 0.01$ | $59.3 \pm 1.12$ | 47 | 49 | 0.55 | 0.57 | 86.24 |
| | $50 \times 10^{-3}$ | $4.00 \pm 0.10$ | $0.58 \pm 0.01$ | $74.2 \pm 1.2$ | 64 | 66 | 0.51 | 0.56 | 127.63 |
| | $66.6 \times 10^{-3}$ | $30.5 \pm 0.79$ | $0.56 \pm 0.002$ | $69.8 \pm 0.32$ | 73 | 75 | 0.17 | 0.17 | 120.5 |
| | $83.3 \times 10^{-3}$ | $32.3 \pm 1.00$ | $0.21 \pm 0.004$ | $66.0 \pm 0.77$ | 81 | 94 | 0.11 | 0.15 | 102.4 |
| Sodium salicylate[d] | 0.00 | $4.30 \pm 0.09$ | $0.13 \pm 0.002$ | $15.6 \pm 0.58$ | 16 | 17 | 0.80 | 0.83 | 543.2 |
| | $8.06 \times 10^{-4}$ | $15.7 \pm 1.1$ | $0.10 \pm 0.002$ | $26.7 \pm 0.57$ | 28 | 26 | 0.25 | 0.16 | 861.6 |
| | $16.1 \times 10^{-4}$ | $15.9 \pm 0.3$ | $0.11 \pm 0.001$ | $65.8 \pm 0.52$ | 123 | 124 | 0.20 | 0.30 | 1094.2 |
| | $32.3 \times 10^{-4}$ | $42.1 \pm 2.4$ | $0.35 \pm 0.01$ | $464.5 \pm 8.2$ | 498 | 450 | 0.05 | 0.10 | 921.5 |
| | $48.4 \times 10^{-4}$ | $45.1 \pm 1.4$ | $0.42 \pm 0.008$ | $308.6 \pm 3.6$ | 262 | 292 | 0.035 | 0.12 | 721.4 |
| | $64.5 \times 10^{-4}$ | $49.5 \pm 2.1$ | $0.48 \pm 0.01$ | $250.3 \pm 3.1$ | 244 | 239 | 0.05 | 0.09 | 518.3 |

Constant reagent concentrations:

[a] $[H_2O_2]=0.051$, [sod]$=1.6\times10^{-3}$ , [Triaz I]$= 1.6\times10^{-4}$  - [b] $[H_2O_2]=0.051$, [sod]$=1.6\times10^{-3}$ , [TCPO]$=3.2\times10^{-3}$

[c] [Triaz I]$= 1.6\times10^{-4}$, [sod]$= 6.4\times10^{-4}$, [TCPO]$=6.4\times10^{-3}$  -  [d] $[H_2O_2]=0.051$, [Triaz I]$= 1.6\times10^{-4}$, [TCPO]$=6.4\times10^{-3}$
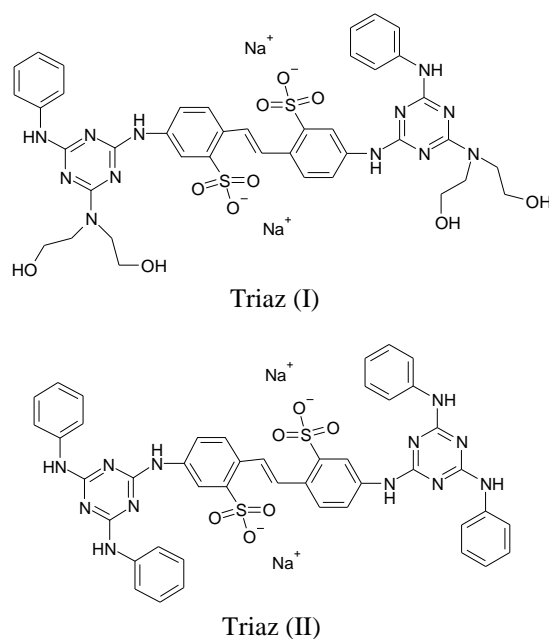
Figure 1. The chemical structures of Triazin I and II.
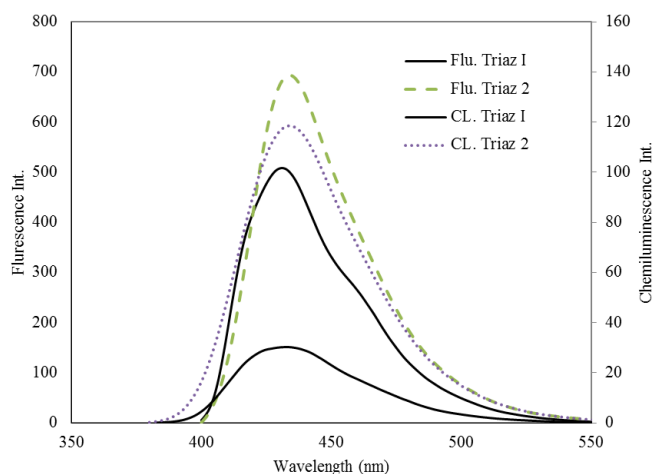


Figure 2. Fluorescence emission and chemiluminescence spectra of Triazin I & II

### 3.1. The effect of reagent concentration on POCL

Application of a steady-state concentration for each of the intermediates is used to solve the complex mechanism for the static PO-CL system. One of the primary parameters in the PO-CL system is the hydrogen peroxide concentration when the object of the chenalysis is the determination of the concentration of fluorescent molecules. In the PO-CL reaction, the rate-determining step is the reaction of oxalate with hydrogen peroxide that is

equal to the rate of the pseudo first-order light decay. In the expressions for the light emission, a linear dependence can be seen in the oxalate concentration and shown in Fig. 3 and 4. Nevertheless, their most important feature is that they increase with increasing oxalate concentration. The quantum yield increased with increasing oxalate concentration.

The effect of Triazinyl concentration, at a constant concentration of TCPO, was studied and

the results are shown in Table 1-2. As it has been clearly shown before, there is an exponential increase in chemiluminescence of the $H_2O_2$-TCPO-Triazinyl system with increasing concentration of the flurophore triazinyl, in the concentration range studied. The influence of varying TCPO concentration in the presence of an excess concentration of $H_2O_2$ was investigated and the results are given in Fig. 3 and 4. As it is seen from Fig. 3 and 4, 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 detail in the literature [19].

The data in Tables 1-2 show the influence of $H_2O_2$ concentration on the PO-CL of triazinyl in the presence of a constant concentration of sodium salicylate. It was found that there is a direct linear relationship between the concentration of hydrogen peroxide and CL intensity of the system as shown in Fig. 3 and 4.

However, in the absence of sodium salicylate, the light intensity at each hydrogen peroxide 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 [6, 19]. In order to investigate the optimal concentration of sodium salicylate, the CL response of the $H_2O_2$-TCPO-Triazazinyl system was measured against the varying concentration of the sodium salicylate and the resulting plot is shown in Fig. 3-4. As it is obvious from Fig. 3-4, the CL intensity sharply increased with increasing concentration of sodium salicylate until a concentration of $3.23 \times 10^{-4}$ M is reached, the observed intensity enhancement being indicative of the catalytic effect of the sodium salicylate. However, further addition of sodium salicylate revealed a gradual decrease of the CL intensity. This is most probably due to the quenching effect of the sodium salicylate at higher concentrations, which begins to decompose of the high energy intermediate, dioxetanedione, and hence the CL light reduces.

In order to study the influence of the nature of base catalysts on the PO-CL of triazinyl, in addition to sodium salicylate, imidazole and some of its derivatives including 4-methylimidazole, 4-methyl-5-nitroimidazole, 4-nitroimidazole, 2,4-dinitroimidazole, 2-hydroxy-4-nitroimidazole, 1-methylimidazole, and 2-thiazomethylimidazole were also examined as potential PO-CL catalysts. It was found that, except with imidazole and 4-methylimidazole, in all other cases the increase in

POCL intensity from $H_2O_2$-TCPO-triazinyl system was too low to be of any analytical interest.

In order to evaluate the kinetic data for the PO-CL system studied from the resulting POCL intensity-time plots, a pooled-intermediate model was used [20-22]. According to this model, the CL reaction is simplified in equation 1.

$$A \xrightarrow{\phantom{x}k_r\phantom{x}} B \xrightarrow{\phantom{x}k_r\phantom{x}} C \qquad (1)$$
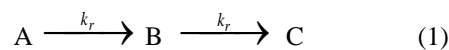
Where A, B and C represent pools of reactants, intermediates and products, respectively, and both reaction steps designated by the rate constants $k_r$ and $k_f$ are irreversible first order reactions. The linear dependence of $Log_{10}I_f$ on the time of chemiluminescence(R=0.9991) proved this model is true in these experiments [23]. The integrated rate equation for the CL intensity versus time is simplified in equation 2.

$$I_t = \left[\frac{M}{(k_f - k_r)}\right]\left[e^{(-k_r t)} - e^{(-k_f t)}\right] \qquad (2)$$

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, 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 ($\tau_{max}$) and the total light yield (Y), as follows:

$$j = M\left(\frac{k_f}{k_r}\right)\left[\frac{k_f}{(k_r - k_f)}\right] \qquad (3)$$

$$\tau_{max} = \frac{\left[\ln\left(\frac{k_f}{k_r}\right)\right]}{(k_f - k_r)} \qquad (4)$$

$$Y = \int_0^\infty I_t dt = \frac{M}{k_f} \qquad (5)$$
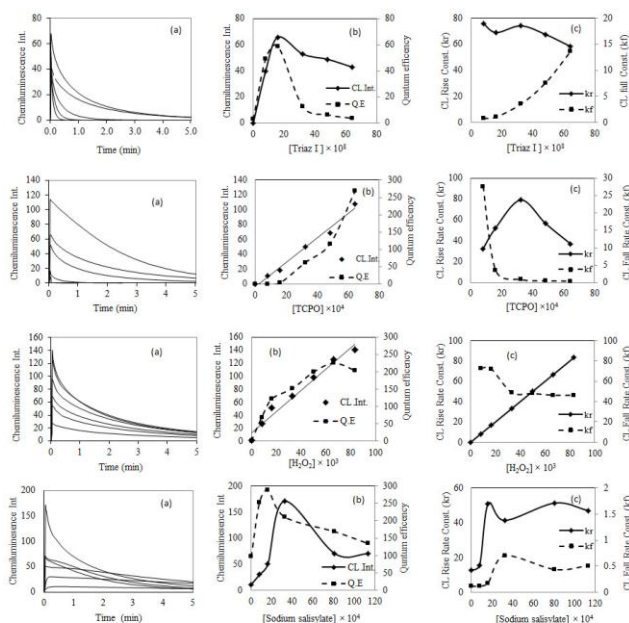
Figure 3. Effect of reagents concentration on the CL intensity(a), quantum efficiency(b), rise and fall rate constant(c) for   POCL of Triazin I (All concentrations and data are tabulated in Tables 1).
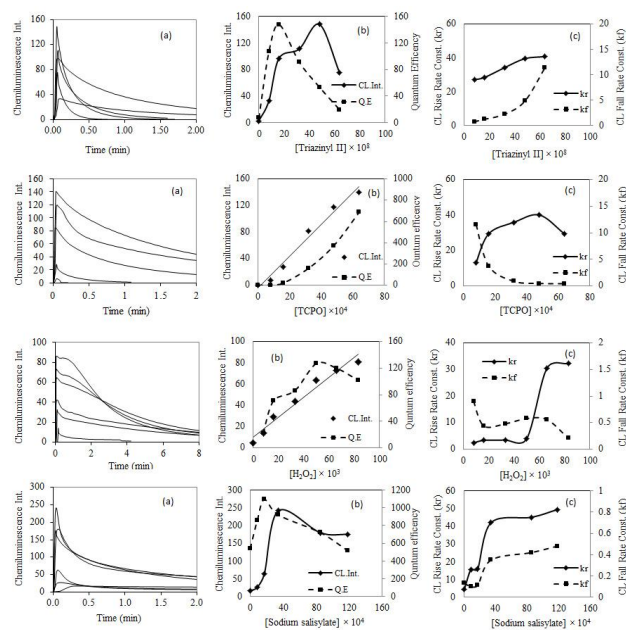


Figure 4. Effect of reagents concentration on the CL intensity(a), quantum efficiency(b), rise and fall rate constant(c) for   POCL of Triazin II (All concentrations and data are tabulated in Tables 2).
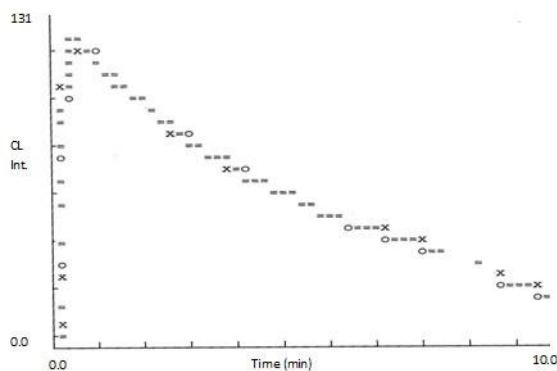
Figure 5. Computer fit of the CL intensity time plot for TCPO-H$_2$O$_2$-Triazinyl-sodium salicylate system: (×) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plot.

Table 3: parameters evaluated from computer fitting of the intensity-time plots for H$_2$O$_2$-TCPO-Triazinyl (I and II) -Base system at various temperatures  [H$_2$O$_2$]=0.06, [TCPO]= 6.4×10$^{-3}$, [Triaz]= 1.6×10$^{-4}$, [sod]= 7.9×10$^{-5}$, [Imi]= 8.4×10$^{-5}$, [4-met-Imi]= 8.4×10$^{-5}$

| Triazinyl | Base | T(K) | $k_r$ (min$^{-1}$) | $k_f$ (min$^{-1}$) | M (μ V) | I (μ V) | $J$ (μ V) | T (min) | $\tau_{max}$ (min) | Y(μ V. min) |
|---|---|---|---|---|---|---|---|---|---|---|
| Triaz (I) | Sodium salicylate | 293 | 14.5 ± 0.09 | 0.13 ± 0.001 | 28.5 ± 0.54 | 27.5 | 27 | 0.300 | 0.323 | 207.4 |
| | | 303 | 17.1 ± 0.15 | 0.18 ± 0.001 | 36.5 ± 0.13 | 35.4 | 35 | 0.250 | 0.267 | 199.8 |
| | | 313 | 24.3 ± 0.31 | 0.23 ± 0.001 | 46.4 ± 0.12 | 44.7 | 45 | 0.135 | 0.175 | 197.4 |
| | Imidazole | 293 | 7.9 ± 0.03 | 0.14 ± 0.005 | 28.9 ± 0.05 | 26.9 | 27 | 0.450 | 0.513 | 203.6 |
| | | 303 | 9.4 ± 0.05 | 0.26 ± 0.001 | 35.5 ± 0.07 | 32.5 | 32 | 0.315 | 0.387 | 133.0 |
| | | 313 | 15.8 ± 0.32 | 0.40 ± 0.005 | 51.6 ± 0.37 | 46.3 | 47 | 0.165 | 0.237 | 127.9 |
| | 4-methyl imidazole | 293 | 19.7 ± 0.08 | 0.15 ± 0.004 | 15.7 ± 0.02 | 15.1 | 15 | 0.207 | 0.248 | 104.2 |
| | | 303 | 22.4 ± 0.47 | 0.17 ± 0.002 | 21.4 ± 0.14 | 20.8 | 21 | 0.173 | 0.213 | 122.0 |
| | | 313 | 23.9 ± 0.34 | 0.22 ± 0.004 | 27.2 ± 0.12 | 26.7 | 26 | 0.163 | 0.201 | 116.2 |
| Triaz (II) | Sodium salicylate | 293 | 13.6 ± 0.25 | 0.15 ± 0.001 | 137.4 ± 0.63 | 131 | 131 | 0.28 | 0.31 | 886.4 |
| | | 303 | 18.3 ± 0.45 | 0.19 ± 0.003 | 159.9 ± 0.75 | 155 | 152 | 0.22 | 0.25 | 815.1 |
| | | 313 | 20.7 ± 0.66 | 0.27 ± 0.004 | 179.5 ± 1.2 | 173 | 173 | 0.14 | 0.21 | 650.1 |
| | Imidazole | 293 | 10.1 ± 0.16 | 0.24 ± 0.002 | 173.4 ± 0.8 | 159 | 158 | 0.31 | 0.37 | 697.6 |
| | | 303 | 12.3 ± 0.21 | 0.31 ± 0.004 | 203.4 ± 1.19 | 183 | 182 | 0.28 | 0.34 | 637.1 |
| | | 313 | 14.3 ± 0.44 | 0.46 ± 0.01 | 272.9 ± 2.2 | 252 | 243 | 0.17 | 0.24 | 581.5 |
| | 4-methyl imidazole | 293 | 11.1 ± 0.16 | 0.16 ± 0.001 | 75.5 ± 0.24 | 71 | 72 | 0.31 | 0.32 | 469.7 |
| | | 303 | 13.2 ± 0.23 | 0.21 ± 0.002 | 93.1 ± 0.41 | 87 | 88 | 0.26 | 0.31 | 534.1 |
| | | 313 | 15.1 ± 0.31 | 0.24 ± 0.004 | 121.2 ± 0.87 | 112 | 111 | 0.22 | 0.30 | 414.8 |

Table 4: Activation parameters obtained from temperature dependence of the fall rate constants for H$_2$O$_2$-TCPO-Triazinyl (I & II)-Base system

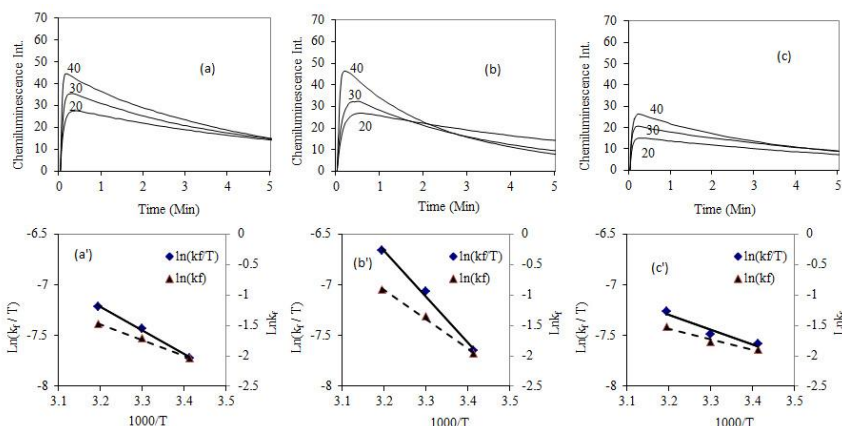| Catalyst | $E_a$ (kJ mol$^{-1}$) | | $\Delta H^{\ddagger}$(kJ mol$^{-1}$) | | $\Delta G$ (kJ mol$^{-1}$) | |
|---|---|---|---|---|---|---|
| | Triazinyl (I) | Triazinyl (II) | Triazinyl (I) | Triazinyl (II) | Triazinyl (I) | Triazinyl (II) |
| Sodium salicylate | 21.75 ± 1.35 | 22.2 ± 2.95 | 19.34 ± 1.37 | 19.81 ± 2.93 | 2.73 ± 0.01 | 5.83 ± 0.02 |
| Imidazole | 40.05 ± 3.37 | 24.72 ± 3.52 | 37.53 ± 3.40 | 22.19 ± 3.49 | 6.77 ± 0.02 | 6.96 ± 0.03 |
| 4-Methylimidazole | 14.52 ± 1.7 | 15.49 ± 2.74 | 12.01 ± 3.17 | 12.98 ± 2.77 | 6.31 ± 0.02 | 5.52 ± 0.02 |

Figure 6. Chemiluminescence intensity, Arrhenius ($\ln(k_f)$ versus $1/T$) and Eyring ($\ln(k_f/T)$ versus $1/T$) plots for TCPO-$H_2O_2$-Triazinyl(I)-sodium salicylate system(a and a'), Imidazol (b and b') and 4-methyl Imidazol (c and c') at 20˚, 30˚ and 40˚C. [$H_2O_2$]=0.06, [TCPO]= $6.4\times10^{-3}$, [Triaz]= $1.6\times10^{-4}$, [sod]= $7.9\times10^{-5}$, [Imi]= $8.4\times10^{-5}$, [4-met-Imi]= $8.4\times10^{-5}$
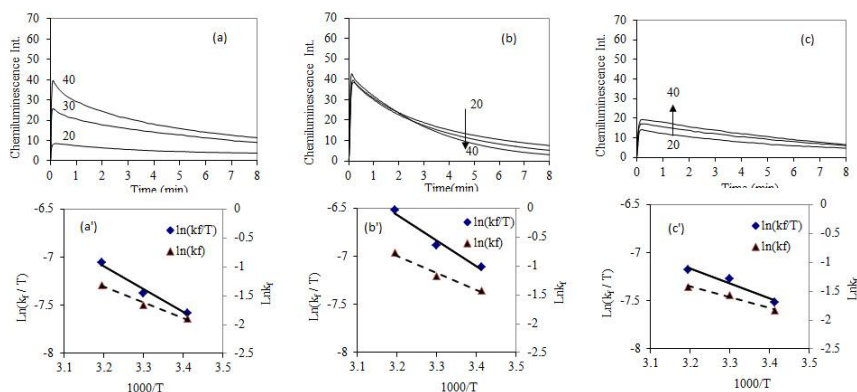


Figure 7. Chemiluminescence intensity, Arrhenius ($\ln(k_f)$ versus $1/T$) and Eyring ($\ln(k_f/T)$ versus $1/T$) plots for TCPO-$H_2O_2$-Triazinyl(II)-sodium salicylate system(a and a'), Imidazol (b and b') and 4-methyl Imidazol (c and c') at 20˚, 30˚ and 40˚C. [$H_2O_2$]=0.06, [TCPO]= $6.4\times10^{-3}$, [Triaz]= $1.6\times10^{-4}$, [sod]= $7.9\times10^{-5}$, [Imi]= $8.4\times10^{-5}$, [4-met-Imi]= $8.4\times10^{-5}$

A typical computer fit of the CL intensity time plots is shown in Fig.5. [24]. In this work, a non-linear least-squares curve fitting program KINFIT was used to evaluate the M, $k_r$ and $k_f$ values from the corresponding CL intensity-time plots[25]. The other parameters J, $\tau_{max}$ and Y were then evaluated from equations (3)–(4) using the $k_r$, $k_f$ and M values. The kinetic parameters thus obtained for all experiments carried out are summarized in table 1and 2.

The CL parameters for the $H_2O_2$-TCPO-Triazinyl system in the presence of sodium salicylate, imidazole and 4-methylimidazole at various temperatures are compared in Table 3. The influence of solution temperature on the chemiluminescence of the $H_2O_2$-TCPO-Triazinyl system, at constant concentration of all reagents involved, in the presence of the three catalysts used was studied. Sample response curves at 20, 30, and 40 °C are shown in Fig. 6 and 7 and resulting CL parameters for the system in the presence of sodium salicylate, imidazole and 4-methylimidazole are summarized in Table 3. Also Fig 6 and 7 illustrates chemiluminescence intensity versus the type of catalyst for triazinyl I and II. As

it is illustrated in Fig. 6-7 and Table 3, in all cases, the PO-CL intensity increased with increasing temperature, due to the enhanced population of the activated triazinyl* molecules also due to the increase of rate of chemical reaction at higher temperatures. However, the decay of light intensity from the maximum occurs at shorter times, as the solution temperature increases. Also quantum efficiency was decreased at higher temperatures as illustrated in tables 3.

The activation energy for the fall step of the PO-CL process was obtained from the slope of the corresponding Arrhenius plot of $\ln k_f$ vs. $1/T$ that is shown in Fig. 6 and 7. Then activation parameters determined in the fall of the PO-CL burst such as $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated by using Eyring transition-state theory from the slope and intercept of the linear plot of $\ln (k_f/T)$ versus $1/T$ [26]. These results are given in Table 4.

## 4. Conclusions

In this paper is showing that activation parameter was depending on the structure and the type of the luminophor and catalyst in peroxyoxalate chemiluminescence systems. The end

result with comparing same study may be stated that: The luminophor and catalyst structure difference is even more, this effect is increased. Also imidazole activation parameters are more than two other catalysts but sodium salisylate have most quantum efficiency than others (Table4). At each temperature the quantum efficiency (Y) is as follows:

Sodium salicylate > imidazole > 4-methylimidazole

This could be an obvious reason for most analytical applications of sodium salicylate as POCL catalyst.

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# تعیین مشخصه های سینتیکی و ترمودینامیکی واکنش نور تابی دو مشتق جدید تری آزین در سیستم پراکسی اگزالات

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**چکیده:**

در این کار نورتابی شیمیایی ناشی از واکنش تری کلرو پر اکسی اگزالات با هیدروژن پراکسید در حضور دو مشتق تری آزین به عنوان لومینوفور بررسی شده است. تاثیر غلظت تری آزین، هیدروژن پراکسید، پراکسی اگزالات، دما، غلظت و نوع کاتالیزور بررسی شده است. مشخصههای سینتیکی نورتابی شیمیایی از طریق مطابقت نتایج تجربی شدت نورتابی- زمان نشر، استخراج شده است. مشخصههای ترمودینامیکی فرایند نظیر انرژی فعالسازی و تابع گیبس فرایند بدست آمده است.

**کلمات کلیدی:** نورتابی شیمیایی پر اکسی اگزالات، تری آزینیل، شفاف کننده های نوری، هیدروژن پراکسید، مشخصه های ترمودینامیکی و سینتیکی

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