

## CHEMILUMINESCENCE PROPERTIES OF PEROXYOXALATE SYSTEM IN ORGANIC SOLVENTS

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## ABSTRACT

Peroxyoxalate system includes an oxalate ester, peroxide and a fluorescer. The energy resulted from the reaction of oxalate ester and peroxide is transferred to fluorescer and cause it to fluorsce. The effect of reactants chemical structure, their concentration, solvent media (polarity and viscosity) and the temperature, on the intensity of the illuminated light with respect to time have been studied. The effect of chemical structure of oxalate ester, fluorescer and peroxide on the intensity of light was found to be as follows:\*\*

DNPO &lt; TCPO &lt; CBPO

BPEN &lt; A &lt; DPA &lt; BPEA

Tert-Butylhydroperoxide &lt; Hydrogen Peroxid

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\*\*DNPO=bis(2,4-dinitrophenyl)oxalate

TCPO=bis(2,4,6-trichlorophenyl)oxalate

CBPO=bis(2,4-dichloro-6-carbobutoxyphenyl)oxalate

BPEA=9,10-bis(phenylethynyl)anthracene

BPEN= $\alpha, \alpha'$ -bis(phenylethynyl)naphthalene

DPA =9,10-diphenyl anthracene

A =Anthracene

## INTRODUCTION

Light can be produced either by incandescence or luminescence. Incandescence arises from the conversion of vibrational energy to radiation energy. All objects having temperatures above zero  $K^{\circ}$  have incandescence property. Luminescence results in from fluorescence or phosphorescence. The former involves electronic transition from singlet to singlet while the latter is the result of electronic transition from triplet to singlet.

The light emitted from a chemical reaction is called chemiluminescence (CL). The energy released from a chemical reaction is transferred to special species and cause their excitation. Upon their return to ground state the excited species then release energy in the form of light[1]. Chemiluminescence has been the subject of many years of investigation. One of the interesting cases is that of the green light emitted from the reaction of lophine with oxygen in the presence of a strong base, first reported by Radziszewski in 1887[2].

Max Trauz reported many examples of CL reactions of several organic compounds with various oxidants in 1905[3]. Kautsky reported the production of a yellow light when a suspension of the siloxen in dilute acid is treated with permanganate[4-6].

Chemiluminescence may occur in solid, liquid or the gas phase. One of

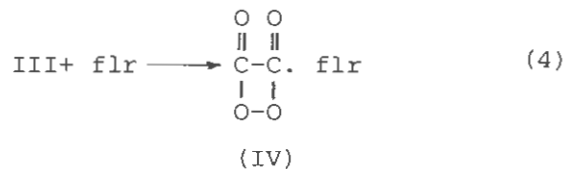
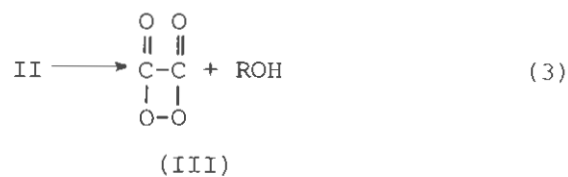
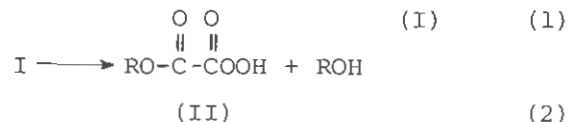
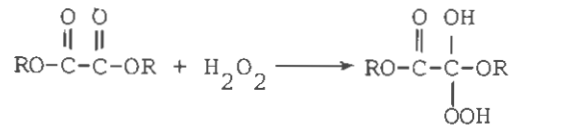
CL reactions in the solid phase, is the oxidation of siloxen with ceric sulfate (or other strong oxidizing agents) which produces a red light [7]. Most of CL reactions however, occur in the liquid phase. Some of these reactions involve the oxidation of phthalhydrazides (e.g. Luminol) or acridinium salts (e.g. Lucigenin) with  $H_2O_2$  in alkaline solutions[8,9]. An example of gas phase CL is the commonly known reaction of white phosphorus vapor with oxygen[10].

In this article we report the CL property of peroxyoxalate system in organic solvents (liquid phase). Another purpose of the research reported here was to elaborate the molecular mechanisms involved in the CL systems studied.

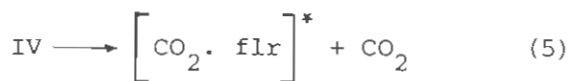
## Peroxyoxalate System:

The CL reaction of peroxyoxalate occurs in the liquid phase. This system includes oxalate ester, hydrogen peroxide and a fluorescer. The reaction of oxalate ester and hydrogen peroxide yields an intermediate which decomposes and produces energy. This energy is subsequently transferred to the fluorescer and causes its excitation. Part of the fluorescer's energy is converted to light, when it returns to its ground state. The wavelength of emitted light depends upon the chemical structure of the fluorescer (usually a polycyclic aromatic molecule). Generally the overall mecha-

nism of CL reaction in the peroxy-oxalate system is proposed as the following [11,12].



flr=fluorescer



## EXPERIMENTAL

### 1. Materials:

Chemicals used were all analytical grade (except for those prepared by ourselves) obtained from chemical suppliers:

Toluene	99% (d=0.86g/ml)
	from Riedel CO.
Ethyl acetate	(d=0.9 g/ml)
	from Riedel Co.
Acetone	99% (d=0.76 g/ml)
	from Merck Co.

Hydrogen peroxide	30% (d=1.1 g/ml)
	from Merck Co.
Chloroform	(d=1.47 g/ml)
	from Fluka Co.
Diethyl phthalate	(d=1.118 g/ml)
	from Fluka Co.
Anthracene	95%
	from Fluka Co.
Dibenzoyl peroxide	from Fluka Co.
Tert-Buthyl hydroperoxide	
80% in Di-tert-buthyl peroxide	
	(d=0.895 g/ml)
	from Fluka Co.
9,10-Diphenyl anthracene	
	99%
	from Aldrich Co.
Carbon tetrachloride	
	99% (d=1.594 g/ml)
	from Fluka Co.
Diethyl phthalate	98% (d=1.118g/ml)
	from Fluka Co.
Bis(2,4,6-trichloro phenyl)oxalate	
	prepared in laboratory Ref[13].
Bis(phenyl ethynyl anthracene)	
	prepared in laboratory Ref[13].
Bis(2,4-dinitro phenyl)oxalate	
	prepared in laboratory Ref[13].
Bis(2,4-dichloro-6-carbobutoxyphenyl)oxalate	
	prepared in laboratory Ref[13].
2. Instruments:	
Cooling bath (alcoholic bath -60°C)	
Kryomat K 90 D.W.	from Lauda Co.
	West Germany.
Spectrofluorimeter	from Hitachi Co.
	Japan.
Melting Point Instrument	Buchi 510

### 3. Measurement of Light intensity:

The intensity of emitted light produced by the reaction of oxalate ester, hydrogen peroxide and fluorescer was measured by a photoresistor. The electrical resistance of photoresistor changes by the intensity of irradiation (electrical resistance decreases as the intensity increases). For this purpose, the sample is placed in front of a photoresistor in a totally dark compartment and its resistance is measured with time. To provide a calibration curve the following experiment is performed.

A photoresistor and six identical green light emitting diodes (LED) are placed at the top and the base of a homemade cone, respectively (LEDs are equally spaced). The number of lighted LEDs increase from one to six and photoresistor's resistance is measured in each case. The variation of resistance with the number of lighted LEDs (Light intensity) is shown in Fig 1.

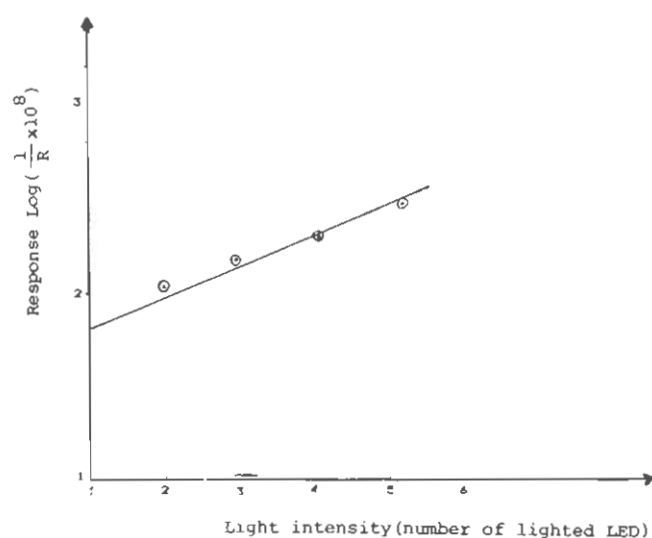


Fig.1: Calibration curve for photoresistor.

All LEDs were alike and produced green light. The current in all LEDs were equal.

R= resistance in Ohms

## RESULTS AND DISCUSSION

The emission lifetime and intensity of CL in the peroxyoxalate system are dependent upon different factors. These factors include: chemical structure of reactants (oxalate ester, peroxide and fluorescer), their concentration, solvent media (viscosity and polarity) and the temperature. The effect of these factors were investigated and the results obtained discussed in the following.

### 1. Effects of chemical structure:

In order to understand the effect of chemical structure, the concentration of reactants and the nature of solvent medium were kept constant and only the composition of reactants were changed.

#### A. Chemical structure of oxalate ester:

The results from the reaction of three oxalate esters (DNPO, TCPO, CBPO) with hydrogen peroxide and BPEA fluorescer which were mixed at a ratio of 1:1:1 are, shown in Fig.2. The in-

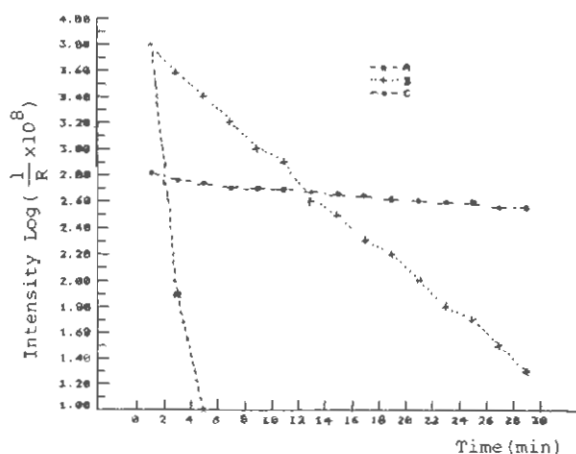


Fig.2: Light intensity vs time for different oxalate esters

A:DNPO      B:TCPO      C:CBPO

oxalate ester= $3.3 \times 10^{-3}$  M

$H_2O_2 = 3.3 \times 10^{-3}$  M

BPEA= $3.3 \times 10^{-5}$  M

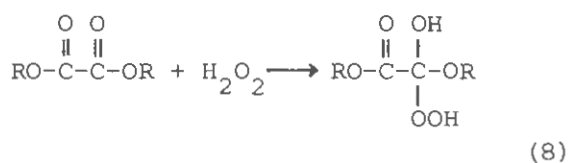
sodium salicylate= $3.3 \times 10^{-6}$  M

solvent:diethyl phthalate

R=resistance in Ohms

tensity and emission lifetime is dependent upon the chemical structure of esters and their corresponding leaving groups. The chemical structure and the leaving groups studied are listed in Table 1.

As shown in Fig.2 at the beginning of the reaction (the first minute) CL intensity is, in the case of DNPO, more than those of CBPO and TCPO; and thereafter there is a steady decrease in all cases. The reason the intensity of CL for one ester is higher than another (at certain time interval) is that the electronegativity of the leaving groups on oxalate esters are different. The positive charge on the carbonyl group is increased by these substituents thereby making it accessible for nucleophilic attack (reaction 8).



As the electronegativity of substituted groups on the benzene ring increases the rate of reaction (8), as well as the intensity of CL for DNPO at a certain elapsed time (e.g. first minute) increases. This is due to the exis-

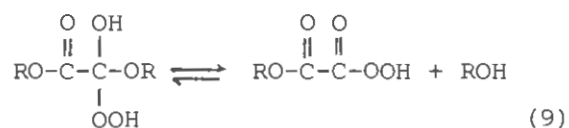
Table 1: The chemical structure of oxalate esters and their corresponding leaving groups

oxalate ester	DNPO	TCPO	CBPO
chemical structure			
leaving group (RO <sup>-</sup> )			

tence of higher electronegative group in DNPO as compared to TCPO and CBPO. The sharp decrease of CL intensity in the case of DNPO is due to its rapid decrease in concentration (high reaction rate). TCPO has a stronger electronegative group than CBPO, thus its CL intensity at the time interval 1-11 minutes is higher than CBPO. The lower intensity of TCPO (after 11 min.) as compared to CBPO is also related to more rapid concentration reduction of TCPO. As shown in Fig.2. The emission lifetime for the three oxalate esters is in the following order:



The emission lifetime increases as the strength of electronegative group decreases. Increasing the electronegativity of substituted groups on phenolate ( $\text{RO}^-$ ) makes it more stable and increases the rate of forward reaction (9).



As mentioned above, the reaction rates of equations (8) and (9) are lower in the case of CBPO, hence a longer emission lifetime (CBPO concentration decreases more slowly).

#### B. Chemical structure of peroxides:

The intensity of emitted light from the reaction of oxalate ester, CBPO, and fluorescer, BPEA, with three peroxides (Hydrogen peroxide, tert-

butyl hydroperoxide, dibenzoyl peroxide) is shown in Fig.3. The intensity of CL for  $\text{H}_2\text{O}_2$  is more than that of tert-butyl hydroperoxide, whereas it was not detectable for dibenzoyl peroxide. The above results can be explained by considering the following reactions. Reaction of  $\text{H}_2\text{O}_2$  and oxalate ester leads to an intermediate (III), as shown below.

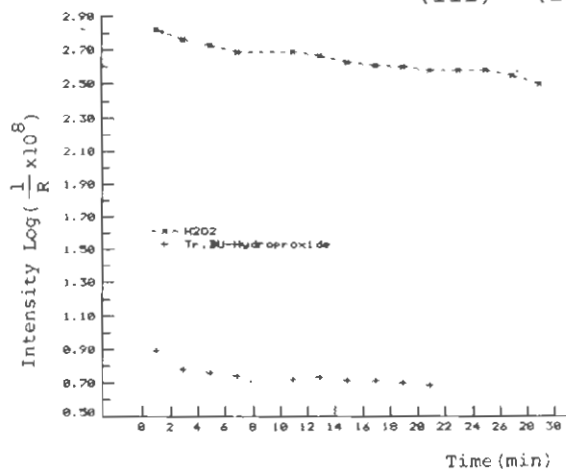
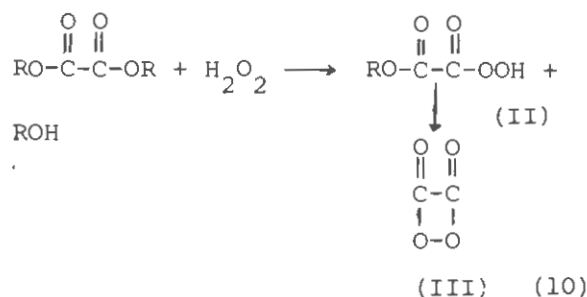


Fig.3: Light intensity vs time for different peroxides.\*

oxalate ester =  $3.3 \times 10^{-3}$  M

$\text{H}_2\text{O}_2 = 3.3 \times 10^{-3}$  M      BPEA =  $3.3 \times 10^{-5}$  M

sodium salicylate =  $3.3 \times 10^{-6}$  M

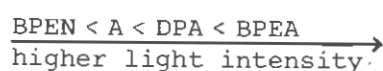
solvent: diethyl phthalate

R = resistance in Ohms

\* Reaction between dibenzoyl peroxide, CBPO, and BPEA does not produce any light.



In aromatic molecules, as the number of rings increases, the energy requirement for electronic transition decreases and consequently the emitted light intensity increases. This expectation is confirmed by experimental results according to the following:

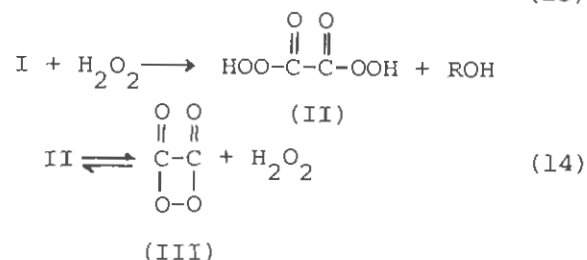
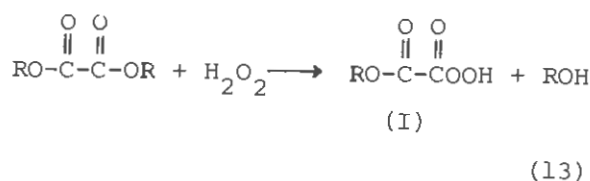


Needless to say the emission spectrum is also varied by the change of fluorescer.

## 2. Effect of concentration:

### A. Concentration of oxalate ester and $\text{H}_2\text{O}_2$ :

As pointed out before, the reaction of oxalate ester and  $\text{H}_2\text{O}_2$  produces the intermediate of 1,2-dioxetanedione (compound III). The concentration of intermediate (III) changes with the change in concentration of the oxalate ester or  $\text{H}_2\text{O}_2$ . For this purpose, the intensity of CL was measured at a constant concentration of both the oxalate ester ( $3.3 \times 10^{-3}$  M) and the fluorescer, whereas that of  $\text{H}_2\text{O}_2$  was varied. If the ratio of  $\text{H}_2\text{O}_2$  concentration to that of the oxalate taken equal to  $K$ , its effect on the CL intensity is found as shown in Fig. 5. At  $K=1$  (concentration of oxalate ester and  $\text{H}_2\text{O}_2$  are equal to  $3.3 \times 10^{-3}$  M) the intensity of emitted light is considerable and there are not much changes at  $K=2, 3, 10$ . For  $K < 1$  reaction (13) is considerable while for  $K > 1$  both reactions of (13) and (14) take place.



At high ( $K > 20$ ) and low ( $K < 1$ ) where lower concentrations of the intermediate (III) are involved the intensity of CL decreases.

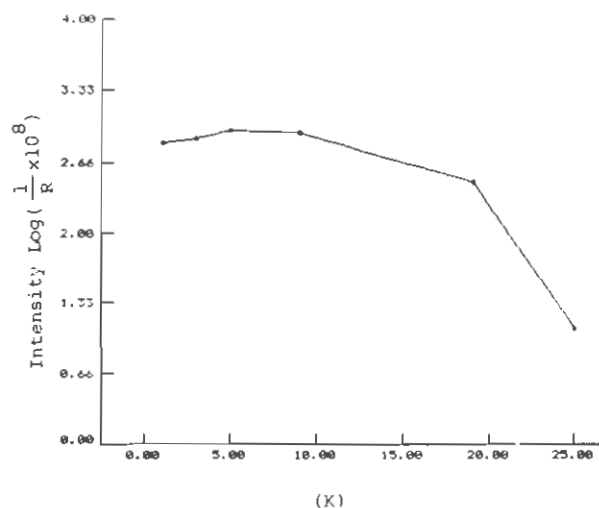


Fig. 5: Light intensity vs molar ratio,

$K$ , of  $\text{H}_2\text{O}_2$  to CBPO  
 BPEA =  $3.3 \times 10^{-5}$  M  
 sodium salicylate =  $3.3 \times 10^{-6}$  M  
 solvent: diethyl phthalate  
 R = resistance in Ohms

### B. Concentration of Fluorescer:

Results of experiments in which the concentration of oxalate ester, CBPO, and hydrogen peroxide are constant while the concentration of fluores -



cer BPEA is varied are shown in Fig. 6. It is clear from Fig.6, that when the concentration of fluorescer is increased more of them become excited and hence the intensity of CL is increased.

### 3. Effect of Solvent:

In this case the effect of polarity and viscosity of solvents are studied.

#### A. Solvent polarity:

The intensity of CL from reaction of CBPO,  $H_2O_2$  and BPEA in carbon tetrachloride, benzene, toluene, chloroform and acetone solvents were measured by photoresistor and their effects shown in Fig.7. The results indicate that

there is no emission in carbon tetrachloride, benzene and toluene, while the intensity of emitted light in acetone is more than that in chloroform. This is due to higher probability of electronic transition of  $\pi \rightarrow \pi^*$  in more polar solvents.

#### B. Solvent viscosity:

Results from CL reaction of oxalate ester, hydrogen peroxide and fluorescer in ethyl acetate, dimethyl phthalate and dioctyl phthalate solvents are shown in Fig.8. The intensity of CL in these solvents is in the following order:

ethyl acetate < dioctyl phthalate < diethyl phthalate

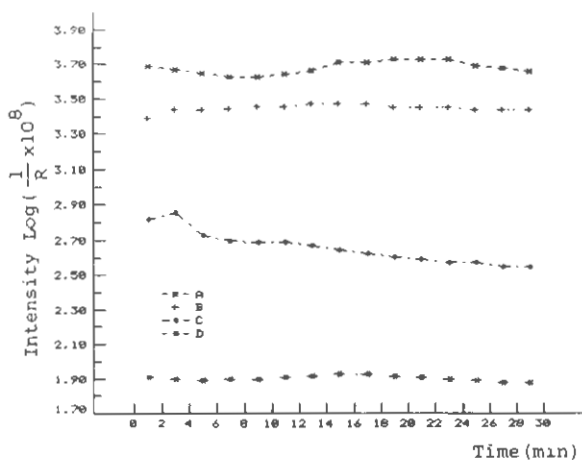


Fig.6: Light intensity vs time for different concentrations of fluorescer BPEA

$$A = 1.6 \times 10^{-4} \text{ M} \quad B = 6.6 \times 10^{-5} \text{ M}$$

$$C = 3.3 \times 10^{-5} \text{ M} \quad D = 1.3 \times 10^{-6} \text{ M}$$

$$\text{oxalate ester} = 3.3 \times 10^{-3} \text{ M}$$

$$H_2O_2 = 3.3 \times 10^{-3} \text{ M}$$

solvent: diethyl phthalate

$$\text{sodium salicylate} = 3.3 \times 10^{-6} \text{ M}$$

R = resistance in Ohms

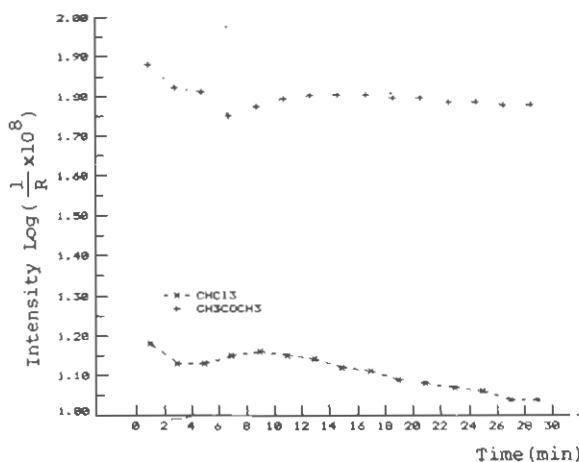


Fig.7: Light intensity vs time for solvents with different polarity

$$\text{oxalate ester} = 3.3 \times 10^{-3} \text{ M}$$

$$H_2O_2 = 3.3 \times 10^{-3} \text{ M}$$

$$BPEA = 3.3 \times 10^{-5} \text{ M}$$

$$\text{sodium salicylate} = 3.3 \times 10^{-6} \text{ M}$$

solvent: diethyl phthalate

R = resistance in Ohms

The probability of external conversion (energy transfer from excited molecule to solvent or other solutes) is less in more viscous solvents thereby leading to a higher CL intensity. Thus, the intensity of CL in solvents with higher viscosity (diethyl phthalate, dioctyl phthalate) is more than those in less viscous solvents (ethyl acetate). Even though the viscosity of dioctyl phthalate is more than that of diethyl phthalate, its CL intensity is lower. This

might be due to the reduction in the numbers of collisions between reactants in the solvents with excessive viscosity.

#### Effect of Temperature:

The effect of temperature for CL reaction of CBPO,  $H_2O_2$  and BPEA was studied in the range between  $-15$  to  $+35^\circ C$ . The results obtained show that as the temperature increases, the intensity of CL increases which might be due to an increase in the rate of CL reaction.

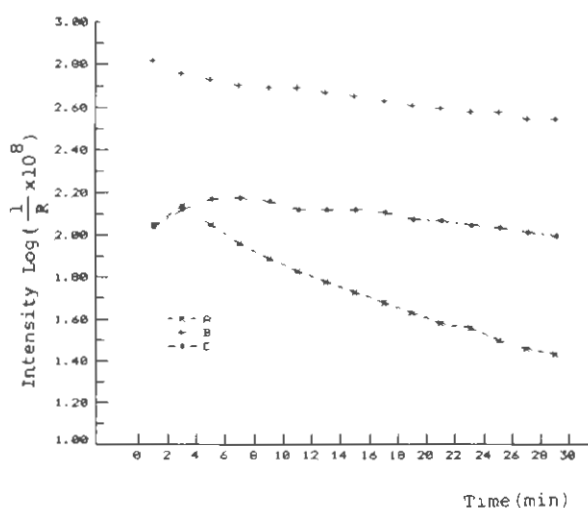


Fig. 8: Light intensity vs time for solvents with different viscosities.

oxalate ester =  $3.3 \times 10^{-3}$  M  
 $H_2O_2 = 3.3 \times 10^{-3}$  M    BPEA =  $3.3 \times 10^{-5}$  M  
 sodium salicylate =  $3.3 \times 10^{-6}$  M  
 solvent: diethyl phthalate  
 R = resistance in Ohms

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