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CHEMILUMINESCENT SYSTEMS - DEVELOPMENT OF HIGH LIGHT CAPACITY FORMULATIONS

Arthur G. Mohan, et al

American Cyanamid Company

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CHEMILUMINESCENT SYSTEMS

DEVELOPMENT OF HIGH LIGHT CAPACITY FORMULATIONS

SUMMARY TECHNICAL REPORT

TO THE

NAVAL WEAPONS CENTER

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13. ABSTRACT

A superior, high performance chemical light system capable of generating 900 lumen hours liter^{-1} of yellow-green light was developed. This formulation, is based on the reaction of H_2O_2 with the oxalate ester bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO) and the fluorescer 1-chloro-9,10-bis(phenylethynyl) anthracene (1-ClBPEA). An efficient green-emitting system (700 lumen hours liter^{-1}) was developed by the use of 2-ClBPEA as the fluorescer. Variation of the catalyst and/or catalyst concentration permits a variety of intensity decay curves to be obtained ranging from bright (2 minutes intensity of 150 foot lamberts cm^{-1}), short-lived reactions to long-lived systems providing a brightness of over two foot lamberts cm^{-1} for 15 hours. The high efficiency of the new system may be related to large spectral shifts which take place in the 1-ClBPEA reactions. Kinetic studies indicate that fluorescer destruction in the chemiluminescent reaction can contribute to light capacity loss at 0.21 M CPPO. This can be overcome by use of stabilizing additives or by increasing the concentration of fluorescer. Storage stability results indicate the relative stability of oxalate components containing different fluorescers is BPEA $>$ 2-ClBPEA $\cong$ 1-ClBPEA $\gg$ 1,5-dichloro BPEA $>$ 1,8-dichloro BPEA. The use of phenolic antioxidants such as 2,6-di-t-butyl-p-cresol permits satisfactory storage stability to be attained with 1-ClBPEA formulations. A study of the effect of storage conditions on the development of induction periods in BPEA oxalate components (0.133 M CPPO) indicates storage at 100°F and 90% relative humidity can produce the induction period in 30 days. Small amounts (7 mole %) of water can be tolerated in the oxalate component, but larger amounts (over 100 mole %) cause immediate formation of induction periods or failure.

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PROJECT SCIENTISTS

PROJECT MANAGER:	DR. MICHAEL M. RAUHUT
PROJECT LEADER :	DR. ARTHUR G. MOHAN

DR. DONALD R. MAULDING
MR. RICHARD L. NARBURGH
MR. ANDREW M. SEMSEL

B

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SUMMARY

A substantially superior second generation oxalate ester chemical light system has been developed. The new system generates three times as much light per unit volume (light capacity) as the first generation system and provides yellow-green emission in contrast to the green emission of the first generation system.

Three modifications of the new system, formulated to meet brightness-lifetime requirements for a variety of applications, are compared with the first generation system in Table A. Relative to the first generation system: (1) the new high intensity formulation is seven times brighter up to 10 minutes of operation for applications which have short lifetime requirements; (2) the new standard formulation is three to four times brighter up to two hours use for intermediate lifetime applications; (3) the long-lived formulation provides a brightness above two foot lamberts cm^{-1} up to 15 hours of use in contrast to less than four hours of useful life for the first generation system. The brightness of the high intensity and standard formulations is adequate for certain illumination applications as well as marking and signaling applications, while the long-lived formulation will accommodate overnight marking.

The color of the new system is visibly more yellow than the green emission of the first generation formulation; the spectral distribution (Figure A) shows a maximum near 550 nm which is close to the optimum wavelength (555 nm) for detection by the human eye. In contrast the first generation, green formulation, has a maximum emission wavelength of 510 nm.

Storage stability data for the oxalate component of the second generation system is summarized in Table B. A light capacity over 600 lumen hours per liter remains after 90 days storage at 75°C in Teflon FEP. Moreover, polyethylene lightsticks containing the new second generation formulation have been shown in a separate program to give acceptable performance after 30 days storage at 75°C (167°F). Lightsticks containing the new formulation are thus expected to meet

military storage criteria, in contrast to first generation lightsticks, which have poor stability at 75°C.

The new system is based on the oxalate ester bis-(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO) and the new fluorescer 1-chloro-9,10-bis-(phenylethynyl)anthracene (1-ClBPEA). The composition of the system is summarized in Table C; a single "oxalate component" is combined with one of three "activator components" selected to give the desired brightness-lifetime performance.

Development of the new system was based on a partial investigation of the relationship of fluorescer structure to inherent chemiluminescence efficiency, resistance to concentration quenching, solubility, and stability. The results of the study indicated that dichloro derivatives of 9,10-bis-(phenylethynyl)anthracene (BPEA) were inherently efficient and, in contrast to BPEA itself, were substantially resistant to efficiency loss at high CPPO concentrations. On the dark side, however, the dichloro BPEA derivatives were found to be less stable than BPEA, and the initial dichloro derivatives, 1,5-DCBPEA and 1,8-DCBPEA were too unstable for practical use. Molecular orbital calculations indicated the theoretical stability order of BPEA type fluorescers to be BPEA $>$ 2-ClBPEA $\cong$ 1-ClBPEA $\gg$ 1,5-DCBPEA $>$ 1,8-DCBPEA (see Table D for abbreviation identifications). Since theory indicated greater stability for the monochloro derivatives 1-ClBPEA and 2-ClBPEA, they were prepared for test. Evaluation showed that the monochloro derivatives were in fact substantially more stable than the dichloro derivatives, and that they retained the high inherent efficiency and resistance to concentration quenching characteristic of the dichloro derivatives. In spite of the superior stabilities of the monochloro derivatives, however, they were still too unstable to meet 75°C, 30-day stability criteria in CPPO chemical light formulations.

Concurrent with the fluorescer design effort, an investigation of stabilizing additives was carried out. It was found that certain phenolic antioxidants, such as 2,6-di *t* butyl-4-methylphenol, were partially effective in stabilizing fluorescers toward destruction both in storage and in the reacting system. The use of such additives with 1-ClBPEA provided sufficient stability for the design of the practical second generation system. Indeed, in the second generation system of Tables A-C, only 10% of the 1-ClBPEA fluorescer is destroyed during a 90-day period at 75°C in Teflon FEP.

A new green fluorescer, 2-ClBPEA, also resulted from the fluorescer study. While not as efficient as 1-ClBPEA, 2-ClBPEA gave light capacities over 700 lumen hours per liter at 0.21 M CPPO. This fluorescer is substantially superior to the first generation fluorescer for applications requiring a bright green color (λ max. 520 nm).

The high efficiency of the second generation system may be related to large spectral shifts which take place during the chemiluminescent reaction. The effect of reaction variables on the rate and extent of spectral change indicates formation of a complex between 1-ClBPEA and a by-product formed at high CPPO concentration may be responsible in part for the increase in efficiency.

Several new oxalate esters were prepared in preliminary efforts to overcome the limiting solubility of CPPO (0.28 M in dibutyl phthalate). Substitution of one or more nitro groups for chlorines in CPPO gave esters which were moderately efficient at .01 M ester concentration, but concentration quenching markedly reduced the efficiency at .10 M with these esters.

A light capacity of 410 lumen hours per liter was obtained from the aliphatic oxalate bis-(2-trichloromethyl-1,1,1,3,3,3-hexafluoro-2-propyl)oxalate (TCHFO) at .10 M concentration using 1-ClBPEA as the fluorescer. Attempts to reduce concentration quenching at 0.20 M TCHFO by substitution of other electron withdrawing groups for the CCl_3 group in TCHFO have been unsuccessful thus far.

A study of the effect of storage conditions on the development of induction periods in BPEA oxalate components indicated that storage at 100°F and 90% relative humidity in polyethylene lightsticks can produce the induction period in 30 days. However, small (<7 mole %) amounts of water in the oxalate can be tolerated without effect on performance. Larger quantities of water (over 100 mole %) cause rapid formation of induction periods or complete failure. A tentative mechanism for the hydrolysis of CPPO is discussed in the text of the report.

In addition to the direct value of providing a substantially superior chemical light formulation, the results of this study indicate substantial promise for the development of still more efficient systems in the future. It is now evident that concentration quenching, which has limited light capacities in the past, can be overcome through proper oxalate ester and fluorescer design and through the use of certain anti-quenching additives. Moreover, the discovery of fluorescer stabilizers permits far wider scope in fluorescer design than has been possible previously.

The second generation system discovered in this study operates at only 0.5% of the theoretical chemiluminescence light capacity. At this level of performance a six-inch second generation lightstick, containing 10g of active ingredients, is equivalent to the light output (9 lumen hours) of a candle burning for 43 minutes and is 5.3 times as efficient on a light output per weight basis (lumen hours per gram) as a size D drycell battery in continuous drain. (The D-cell weighs 86g and generates 15 lumen hours of light in continuous drain). We believe that a system capable of operating at two to 10 times the efficiency of the new second generation system (up to 5% of the theoretical limit) is feasible, and it is evident that such a third generation system would provide a major benefit in terms of brightness-lifetime performance and portability characteristics.

Table A

Comparative Performance of Chemical Light Systems

Operating Time (Min.)	1st Generation Formulation	Second Generation Formulations		
		High Intensity	Standard	Long-Lived
2	20.5	151.	79.5	12.9
10	16.0	117.	72.2	13.7
30	12.6	67.6	51.3	11.6
60	7.9	31.9	31.6	9.6
90	5.9	9.4	19.6	8.0
120	4.3	3.2	11.4	9.6
180	2.5	0.6	4.6	7.2
240	----	0.1	2.4	6.2
15 Hours	----	-----	----	2.1
Lt. Cap. (Lm.Hrs.l.$^{-1}$)	290	880	883	888

Table B

Storage Stability of Oxalate Components Containing CPPO and 1-ClBPEA at 75°C in Teflon FEP

Days Stored	% 1-ClBPEA Remaining[b]	% of Initial Lt. Cap.	Lt. Cap.	Q. Y.[d] x 10^2	T.75	Intensity (Ft. Lambert cm^{-1}) vs. Time (Min.)							
						2	10	30	60	90	120	180	240
0	--	--	940	14.7	105	71.1	70.8	53.3	34.0	23.4	15.3	6.0	2.8
14	--	98	918	14.3	97	78.9	74.0	52.8	34.2	21.4	12.9	5.1	2.5
28	90	90	842	13.2	71	94.1	84.6	56.7	33.0	16.6	8.3	3.0	1.4
42	97	86	807	12.6	75	96.0	87.5	52.3	26.7	14.9	8.4	3.1	1.6
60	87	78	736	11.5	70	93.7	63.9	47.6	33.0	15.0	7.0	2.3	1.0
90	89	64	604	9.44	108	55.1	42.7	31.4	20.5	15.6	10.3	4.4	2.0

a. Stored oxalate component contained .28 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), 10.67 x 10^{-3} M 1-chloro-9,10-bis(phenylethynyl)anthracene (1-ClBPEA) and .001 M 2,6-di-*t*-butyl-p-cresol in dibutyl phthalate. Chemiluminescent reactions were run against a single sample of the activator component (3 vols. oxalate/ 1 vol. of activator) which contained .002 M sodium salicylate and 1.5 M H_2O_2 in a solvent of 80% (by volume) of dimethyl phthalate, 20% t-butanol.

b. As determined by absorption spectrum.

c. Light capacity in lumen hours $liter^{-1}$.

d. Quantum yield in einsteins $mole^{-1}$.

Table C

Composition of Second Generation System

Oxalate Component (3 parts by volume)

Material	Concentration M	Concentration g/l
Bis-(2,4,5-Trichloro-6-carbopentoxy-phenyl)Oxalate (CPPO)	0.280	189.6
1-Chloro-9,10-bis(phenylethynyl) Anthracene (1-ClBPEA)	1.067×10^{-2}	4.406g
2,6-Di-t-butyl-p-cresol	0.001	0.220
Dibutyl Phthalate	SOLVENT	

Standard Activator Component (1 part by volume)

Material	Concentration M	Concentration g/l
Hydrogen Peroxide	1.5	51.0
Sodium Salicylate*	2×10^{-3}	0.320
80% (by volume) Dimethyl phthalate 20% (by volume) t-Butanol	SOLVENT	

*The high intensity formulation contains 4×10^{-3} M (0.640 g/l) of sodium salicylate and the long-lived formulation contains 4×10^{-4} M (0.126 g/l) of tetramethylammonium 3,5,6-trichlorosalicylate.

Table D
Identification of Fluorescers and Oxalate Esters

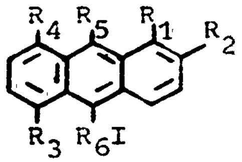
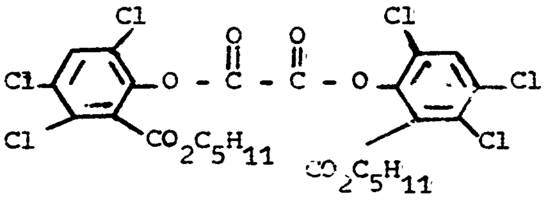
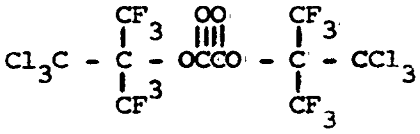
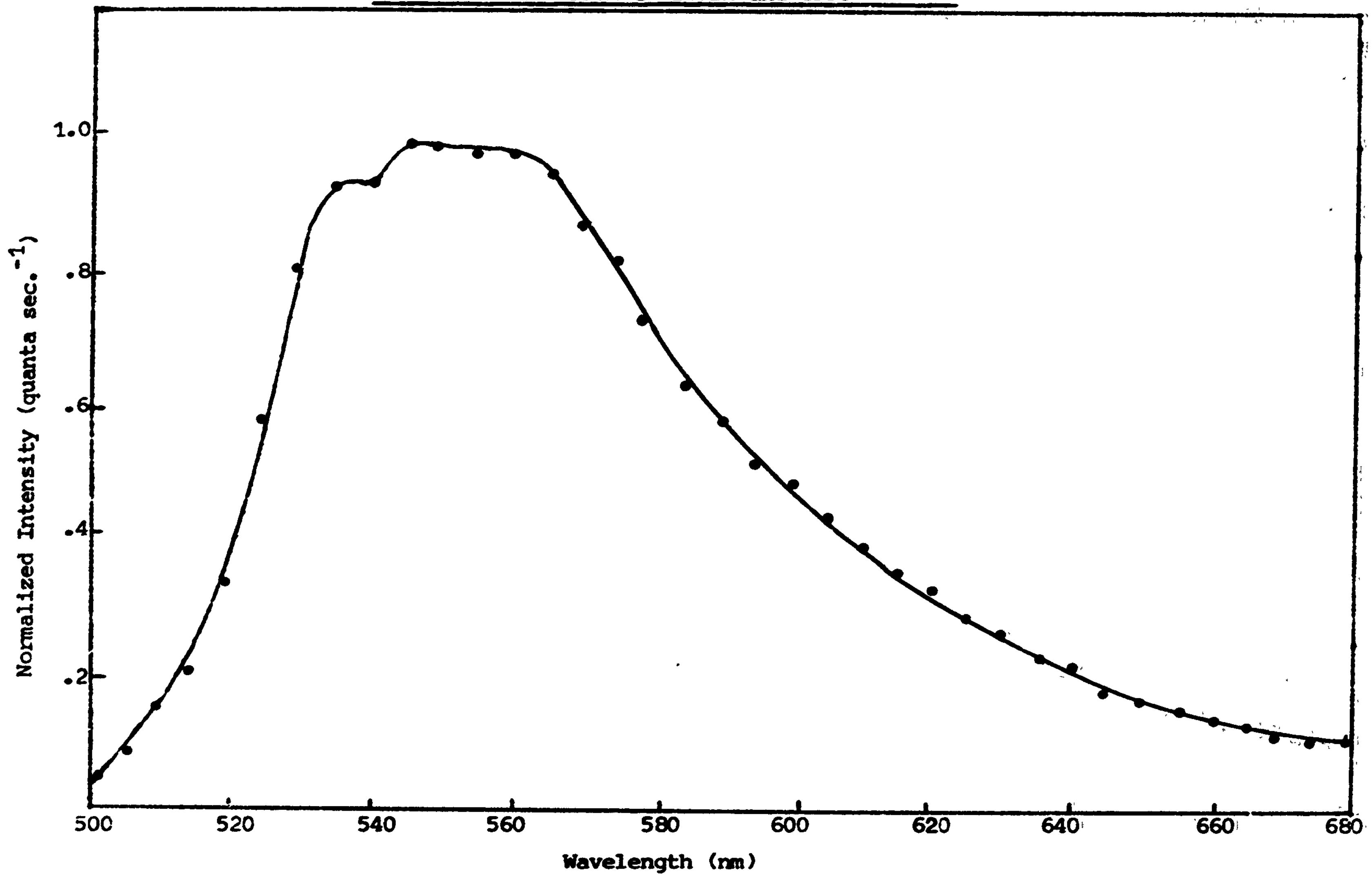
Abbreviation	Name	Structure
		
BPEA	9,10-Bis(phenylethynyl)anthracene	I: $R_1=R_2=R_3=R_4=H$; $R_5=R_6=$ PhC ≡ C
1-ClBPEA	1-Chloro-9,10-bis(phenylethynyl)anthracene	I: $R_1=Cl$; $R_2=R_3=R_4=H$; $R_5=R_6=$ PhC ≡ C
2-ClBPEA	2-Chloro-9,10-bis(phenylethynyl)anthracene	I: $R_1=R_3=R_4=H$; $R_2=Cl$; $R_5=R_6=$ PhC ≡ C
1,5-DCBPEA	1,5-Dichloro-9,10-bis(phenylethynyl)anthracene	I: $R_1=R_3=Cl$; $R_2=R_4=H$; $R_5=R_6=$ PhC ≡ C
1,8-DCBPEA	1,8-Dichloro-9,10-bis(phenylethynyl)anthracene	I: $R_1=R_4=Cl$; $R_2=R_3=H$; $R_5=R_6=$ PhC ≡ C
CPPO	Bis-(2,4,5-trichloro-6-carbopentoxyphenyl) oxalate	
TCHFO	Bis(2-trichloromethyl-1,1,1,3,3,3-hexafluoro-2-propyl)oxalate	 $Cl_3C-C(CF_3)_2-OCCO-C(CF_3)_2-CCl_3$

Figure A

Spectral Distribution of the Chemiluminescent Emission from 1-ClBPEA and CPPO^a



Footnotes to Figure A

a. The chemiluminescent reaction contained 0.21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), 0.375 M H_2O_2, .008 M 1-chloro-9,10-bis(phenylethynyl)anthracene (1-ClBPEA) and 5 x 10^{-4} M sodium salicylate in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol. The spectrum was recorded two hours after the initiation of the reaction and is corrected for the intensity decay.

I. PROGRAM OBJECTIVE

The objective of this research program was the development of high performance oxalate chemical lighting systems comprising both high light capacity and high curve shape efficiency. The first generation system[1,2,3] based on the reaction of bis(2,4,5-trichloro-6-carbopentoxyphenyl) oxalate (CPPO) and hydrogen peroxide with 9,10-bis(phenylethynyl)anthracene (BPEA) as the fluorescer has a practical light capacity limit of about 350-400 lumen hours liter^{-1} because of a decrease in efficiency which takes place with increasing concentration of the oxalate ester, CPPO. The factors causing this concentration quenching have been partially established in previous studies[2,3] and these results have been applied to the development of a practical high light capacity second generation system.

II. INTRODUCTION

The American Cyanamid Company has conducted research on chemiluminescence since 1961 with Government sponsorship beginning on June 1, 1963. Work under the initial contract, Nonr 4200(00), funded by the Advanced Research Projects Agency and administered by the Office of Naval Research, was principally concerned with fundamental investigations of chemiluminescence mechanisms and was directed toward the discovery of the basic knowledge required for the design of practically useful chemiluminescent reactions. Basic knowledge developed under that contract resulted in the discovery of "Peroxyoxalate Chemiluminescence", a group of mechanistically related reactions inherently capable of high light emission efficiencies.[1]

While peroxyoxalate chemiluminescence was inherently efficient, it was clear that a substantial effort would be required to develop the reaction into a practical lighting system. Major problems dealing with the design of specific oxalates and fluorescers and with the selection of catalysts and solvents required for the formulation of an easily used system meeting performance, storage stability and other practical requirements had to be solved. This task was successfully accomplished under Contract N60921-67-C-0214, funded by the Naval Ordnance Systems Command under contract with the Naval Ordnance Laboratory.[2] Under that contract a first generation practical, two-component chemical lighting system was developed (see Table A).

The results of the initial Naval Ordnance Laboratory Program indicated that a substantial increase in light output, which was needed for broad utility, would be a formidable task because of "concentration quenching" effects discussed in Section III. A second program was undertaken with the Naval Ordnance Laboratory under Contract N60921-70-C-0198 to establsh design criteria which would overcome the concentration quenching obstacle.[3] Discoveries in that program indicated that the prospects for development of a superior system were promising, and the program summarized in this report was undertaken with the Naval Weapons Center to fulfill that promise.

III. CONCEPTS AND BACKGROUND

The performance of chemical lighting formulations is measured in terms of the light capacity.

The light capacity is the integrated output of visual light per unit volume, as defined in equation 1.

$$L = \int_{T=0}^{T=\infty} \frac{I\,dt}{V} \qquad (1)$$

In equation 1, I is the luminous flux in lumens, T is time in hours and V is the volume of the formulation in liters. The light capacity, L, has the units of lumen hours per liter. It follows from equation 1 that increased light capacity will provide (1) greater brightness over a given lifetime, (2) longer lifetime at a given brightness level and (3) lower bulk, i.e., more lumens hours per unit weight or volume.

The light capacity is dependent on the factors indicated in equation 2.[2]

$$L = 4.07 \times 10^4 \times Q\ C\ P \qquad (2)$$

Q is the quantum yield in einsteins mole^{-1} of limiting reactant; C is the concentration of limiting reactant in moles liter^{-1}; and P is a photopic factor, varying from 0 to 1, which defines the sensitivity of the human eye to the color of the emitted light. In principle, one molecule of reactant can generate one quantum of light, and one mole of reactant can generate one einstein. Thus quantum yields of one are possible in theory. In practice, however, quantum yields of the most efficient classical chemiluminescent reactions are only about 0.01. The concentration of limiting reactant might, in principle, be as high as about 5 moles liter^{-1}, as for example, in a two reactant system where each reactant has a density of one and a molecular weight of 100. In practice, however, high quantum yields usually require relatively low reactant concentrations. The photopic factor would be a maximum of 1.0 for a yellow line emitter at 555 mμ, at the optimum wavelength for eye sensitivity. In practice, however, chemiluminescent emitters have broad spectral distributions and the maximum practical protopic factor is about 0.86. The photopic factor decreases rapidly toward the blue and red ends of the visible spectrum, the lower P factor must be compensated by higher Q or C factors to maintain the same brightness and lifetime.

The light capacity of the CPPO-BPEA chemical lighting formulation is put into perspective in Table 1. While this oxalate system is considerably more than effective than the most efficient reactions known at the start of this program, its light capacity still represents less than 0.2 percent of the theoretical chemiluminescence potential. As indicated in Table 1, light capacity improvement is possible both through increases in quantum yield and through higher reactant concentrations. Quantum yields as high as 28% have been obtained from peroxyoxalate chemiluminescent reactions,[1] thus a goal of 9000 lumen hours liter^{-1} seems reasonable for an oxalate chemiluminescent system. The data summarized in Table 1 clearly illustrate that the greatest potential for large increases in light capacity over the CPPO-BPEA system lies in increasing the concentration of the limiting reactant, the oxalate ester. As the concentration of the oxalate ester is increased, however, a loss in efficiency, termed "concentration quenching", generally results. With the development of more soluble oxalate esters such as CPPO, the efficiency loss was found to be substantial above .10 <u>M</u>. Typically[4], the CPPO-BPEA system gives a 9% quantum yield at .10 <u>M</u> CPPO, (a light capacity of 260). However, at .20 <u>M</u> the quantum yield drops to 4%, (light capacity 220) and at .30 <u>M</u> CPPO the efficiency is only 1.7% (light capacity 147). Since the light capacity is proportional to the oxalate concentration, in the absence of quenching effects, one would have expected a three fold increase in light capacity by increasing the CPPO concentration from .10 <u>M</u> to .30 <u>M</u>.

Concentration quenching in a chemiluminescent reaction, in principle, can include two general classes of quenching mechanisms: chemical quenching and fluorescence quenching.

Chemical quenching is an interference with any of the chemical reaction steps leading to the generation of the excited fluorescer. Chemical quenching thus involves side reactions which divert chemiluminescent intermediates from the chemiluminescent reaction path. Typical side reactions would be hydrolysis of the oxalate <u>1</u>, decomposition of the monoperoxy acid <u>2</u>(liberating carbon monoxide and

Table 1

Light Capacity: Progress and Potential

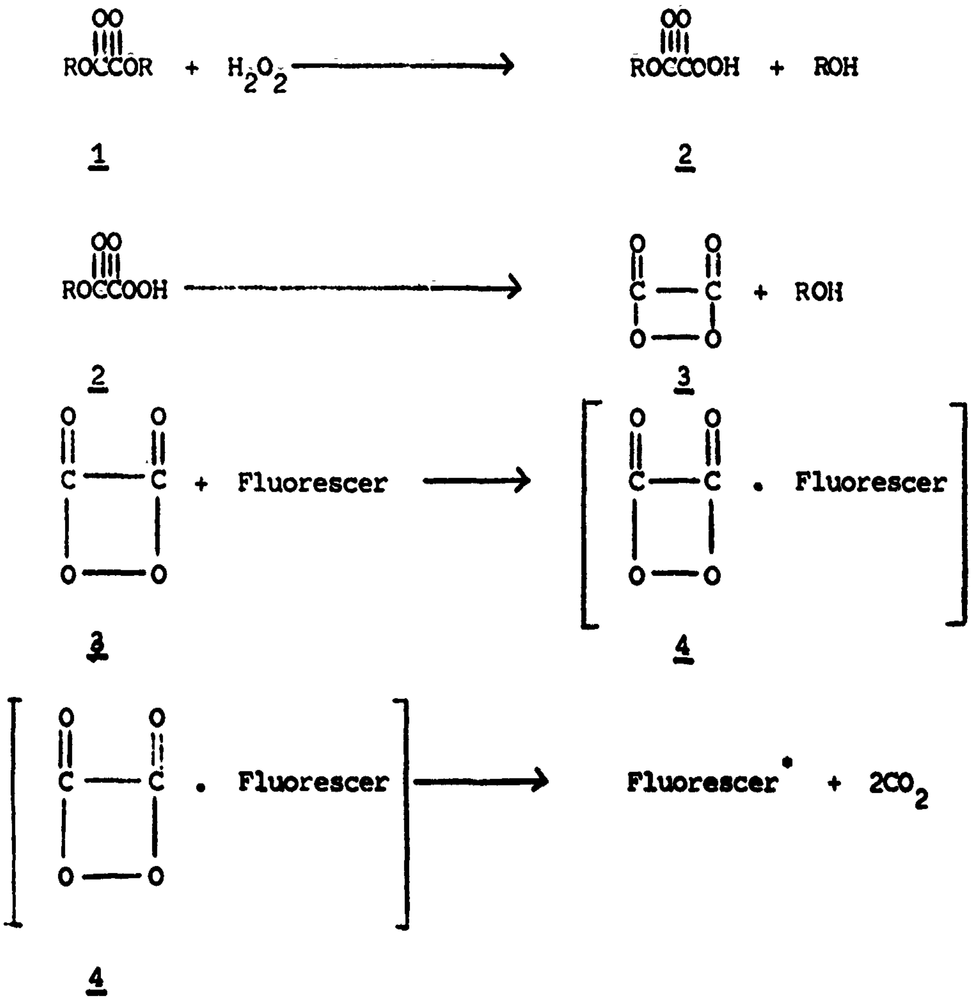
	L	=	Q	·	C	·	P	x	4.07×10^4	Percent of Theory
Luminol - Persulfate[a]	0.2		.004		.008		.12			0.0001
Luminol - Persulfate Fluorescein[b]	1.3		.004		.008		.86			0.0007
CPPO - BPEA	327		.11		.10		.73			0.19
CPPO - 1-ClBPEA	940		.15		.21		.75			0.54
Reasonable Goal	9,100		.28		1.0		.80			5.2
Theoretical Potential	175,000		1.0		5.0		.86			100.

a. Reaction of 3-aminophthalhydrazide, hydrogen peroxide and potassium persulfate in aqueous sodium carbonate solution.

b. As in (a) with sodium fluorescein added.

carbon dioxide, and decomposition of the dioxetandione 3.

Chart I



The key intermediate, 3, can decompose either by a unimolecular pathway dependent only on the concentration of 3 or by second (or higher) order processes dependent on the concentration of 3 and some other species present in the reaction mixture. Since the formation of the fluorescer-dioxetandione complex 4 is a bimolecular process, the second order decomposition of 3 should be "swamped out" by increases in the fluorescer concentration.

Recent evidence[5] obtained by stopped flow kinetic measurements suggests that the reaction of the key chemiluminescent intermediate with the fluorescer to produce light is very rapid relative to the preceeding steps.

Fluorescence quenching is any non-radiative de-excitation of the excited fluorescer. This results from the interaction of the excited molecule with another species in the system. In general the fluorescence quencher can be pictured[6] as a substance which robs the energy rich singlet state molecule of its energy, the energy then being released as heat.

A detailed study of concentration quenching processes revealed that in the BPEA-CPPO system approximately equal contributions from fluorescence quenching and chemical quenching were responsible for the efficiency loss. Structure-fluorescence quenching correlations with a number of substituted BPEA derivatives indicated that substitution of chlorine atoms on the anthracene ring substantially reduced fluorescence quenching by CPPO. The use of certain polymeric additives apparently reduced chemical quenching as well.

IV. INVESTIGATIONS OF NEW FLUORESCERS

A. Design and Synthesis

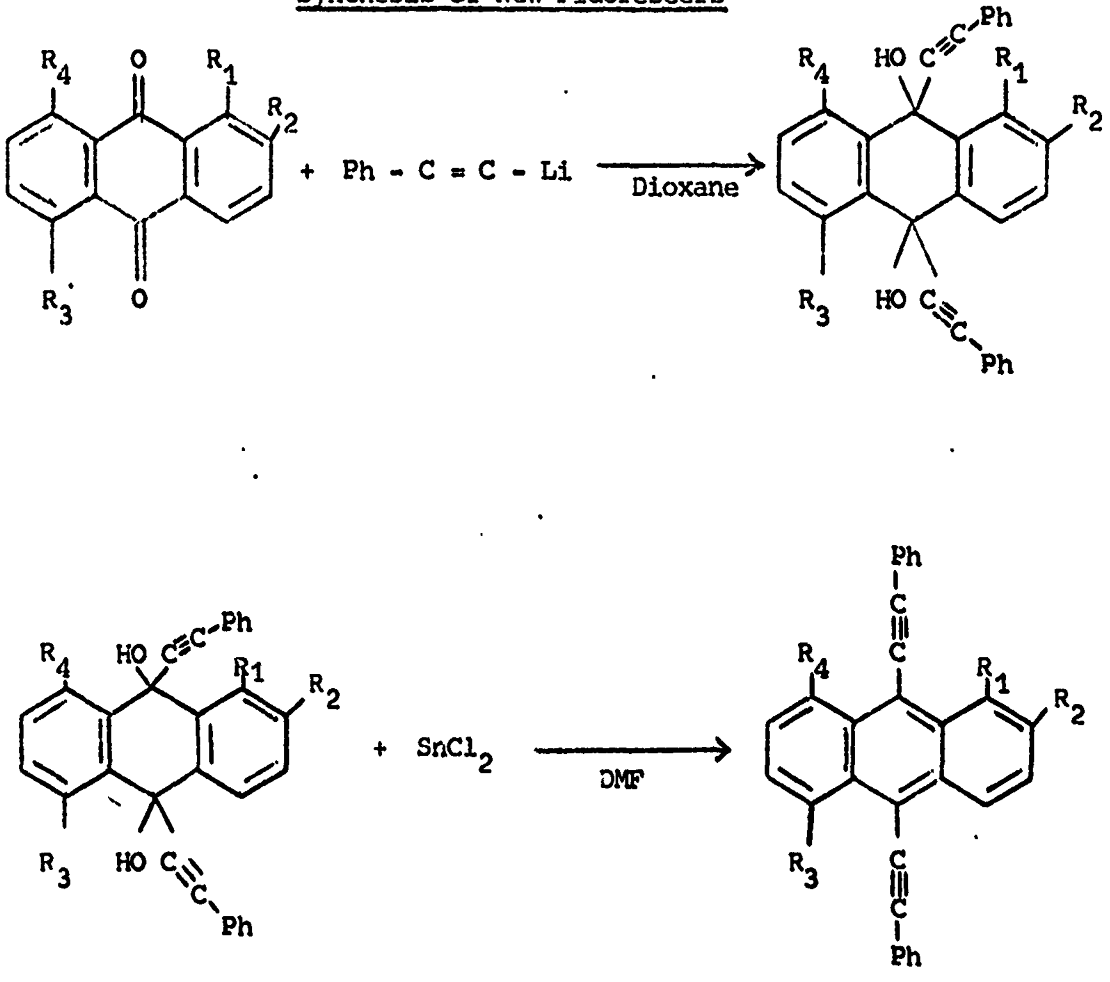
Experiments carried out under the Naval Ordnance Laboratory contract[3] indicated that 1,5-dichloro-9,10-bis(phenylethynyl)anthracene (1,5-DCBPEA) was resistant to fluorescence quenching by CPPO and moderately efficient in the chemiluminescent reaction. However, this compound was not sufficiently soluble (maximum solubility in dibutyl phthalate is 1.8×10^{-3}) to obtain the optimum performance from the chemiluminescent system. The synthesis of a series of chlorinated derivatives of BPEA was undertaken in an effort to find a more soluble analog of 1,5-DCBPEA which maintained its resistance to fluorescence quenching by CPPO and high efficiency in the chemiluminescent reaction.

The synthetic scheme outlined in Chart II was used for the synthesis of all the flourescers. The products were purified by recrystallization, and purity was verified by absorption spectra, thin layer chromatography and elemental analysis.[7,8]

Synthesis of 1,4,5,8-tetrachloro-9,10-bis(phenylethynyl)anthracene was attempted[7] but the pure material could not be isolated from the crude product mixture. Qualitative chemiluminescent tests with the impure material indicated it gives an orange emission when treated with H_2O_2 and CPPO.

Chart II

Synthesis of New Fluorescers



1-Chloro-9,10-bis(phenylethynyl)anthracene (1-ClBPEA): R_1 = Cl; R_2,R_3,R_4 = H.

2-Chloro-9,10-bis(phenylethynyl)anthracene (2-ClBPEA): R_2 = Cl; R_1,R_3,R_4 = H.

1,5-Dichloro-9,10-bis(phenylethynyl)anthracene (1,5-DCBPEA): R_1,R_3 = Cl; R_2,R_4 = H.

1,8-Dichloro-9,10-bis(phenylethynyl)anthracene (1,8-DCBPEA): R_1,R_4 = Cl; R_2,R_3 = H.

B. Chemiluminescent Performance of 1,5- and 1,8-DCBPEA

The solubility of 1,8-DCBPEA in dibutyl phthalate is quite good; oxalate components containing 1.3 x 10^{-2} M 1,8-DCBPEA can be prepared readily. The spectral distribution of the chemiluminescent emission from 1,8-DCBPEA is shown in Figure 1. The maximum of the spectral distribution is observed at 565 nm with a photopic factor of 0.70 at the optimum concentration of fluorescer in the chemiluminescent reaction. The color of the emitted light is a bright yellow. A Stern-Volmer quenching study (Table 2) indicated that CPPO does not quench the fluorescence of 1,8-DCBPEA to any significant degree at the solubility limit of the oxalate.

Table 2

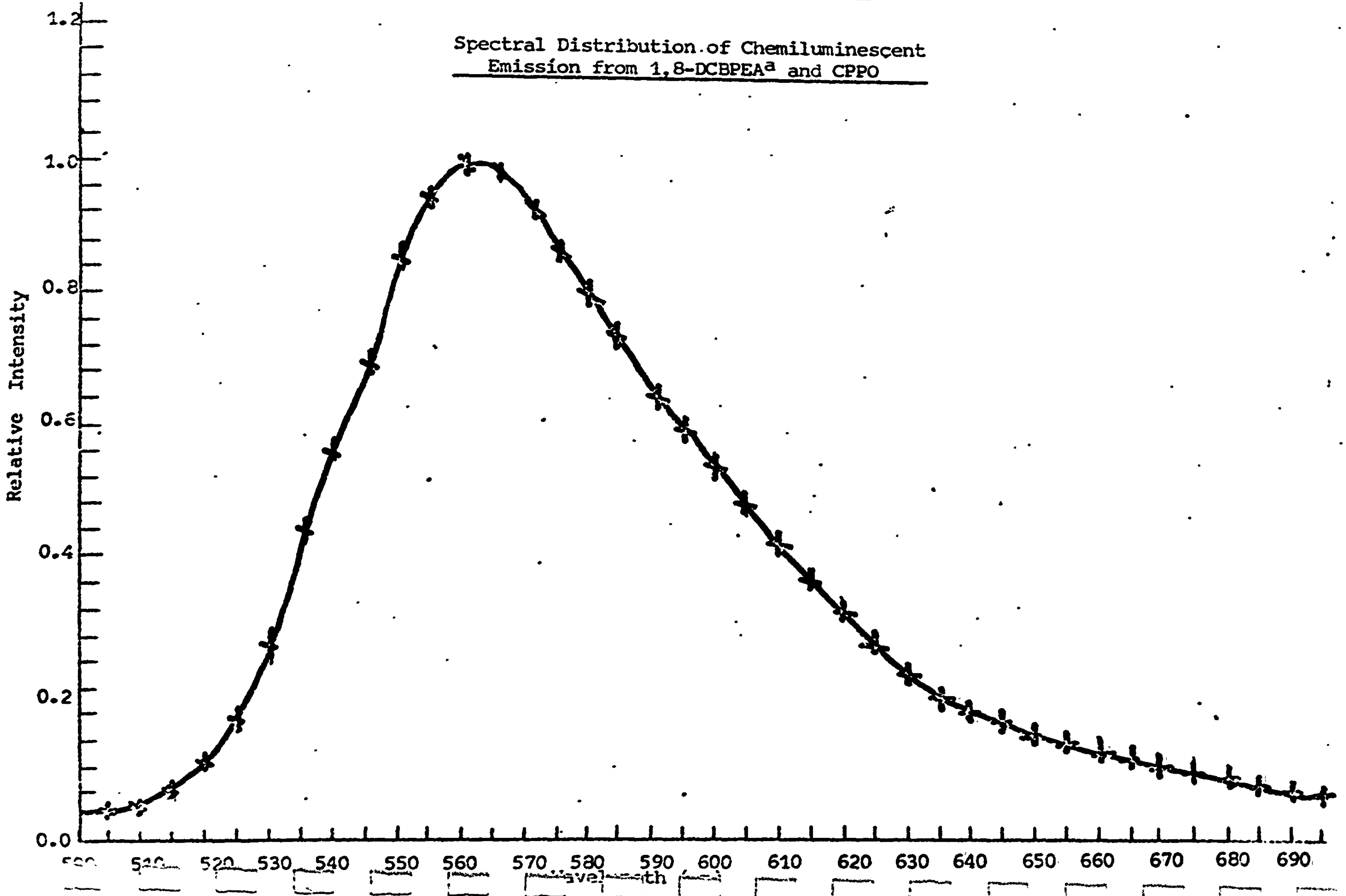
Fluorescence Quenching Experiments with 1,8-DCBPEA and CPPO

CPPO M	F[a]
0	0.930
0.28	0.944

a. Fluorescence quantum yield. Excitation wavelength was 429 nm. Solvent was dibutyl phthalate. The concentration of 1,8-DCBPEA was 4.54 x 10^{-3} M.

The initial set of chemiluminescent experiments using 1,8-DCBPEA and 0.21 M CPPO is reported in Table 3. This set of experiments was designed to determine the optimum concentration of the fluorescer. This optimum was determined to be 5.67 x 10^{-3} M since no significant change in the efficiency of the chemiluminescent reaction was evident above this concentration. The three lower concentrations of 1,8-DCBPEA gave significantly lower brightness levels starting at 180 minutes. It seemed likely that fluorescer decomposition was contributing to the efficiency loss in the later stages of the chemiluminescent reaction. Independent measurement of the fluorescer decomposition rates (see Section IV-F)

Figure 1



Spectral Distribution of Chemiluminescent Emission from 1,8-DCBPEA^a and CPPO

Footnotes for Figure 1

a. Chemiluminescent reaction contained 3.41×10^{-3} M 1,8-dichloro-9,10-bis(phenylethynyl)anthracene (1,8-DCBPEA), 0.21 M bis-(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), 1.56×10^{-4} M sodium salicylate and 0.375 M hydrogen peroxide in a solvent of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol. Intensity scale is in relative quanta sec.$^{-1}$. Spectrum is corrected for intensity decay.

Table 3

Effect of 1,8-DCBPEA Concentration on Chemiluminescence Efficiency at 0.21 M CPPO[a]

1,8-DCBPEA M x 10^3	Q. Y.[b] x 10^2	Lt. Cap.[c]	T.75[d]	Intensity (Ft. Lbt. cm^{-1}) vs. Time (min.)						
				2	10	30	60	120	180	240
7.94	7.76	478.	163.	33.4	24.4	15.0	11.3	7.8	5.2	2.4
6.80	7.74	457	146	38.7	28.4	18.0	13.5	9.0	5.7	3.7
5.67	7.70	463	142	42.2	29.9	18.8	14.0	9.0	5.4	3.2
4.53	5.97	363	110	38.4	27.8	16.9	12.3	7.2	2.8	1.1
3.40	5.89	369	91	46.6	31.4	18.6	13.6	6.3	2.2	0.6
2.27	4.11	261	59	45.1	30.2	17.1	10.1	2.0	0.2	0.1

[a] Chemiluminescent reaction contained 0.21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl) oxalate (CPPO), 1.56 x 10^{-4} M sodium salicylate, 0.375 M H_2O_2 and the indicated concentration of 1,8-dichloro-9,10-bis(phenylethynyl)anthracene (1,8-DCBPEA) in a solvent of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol.

[b] Quantum yield in einsteins $mole^{-1}$.

[c] Light capacity in lumen hours $liter^{-1}$.

[d] Time (minutes) required for emission of 75% of the total amount of light.

Table 4

Effect of 1,8-DCBPEA Concentration on Chemiluminescence Efficiency at 0.10 M CPPO[a]

1,8-DCBPEA M x 10^3	Q. Y.[b] x 10^2	Lt. Cap.[c]	T.75[d]	Intensity (Ft. Lmbt. cm^{-1}) vs. Time (min.)						
				2	10	30	60	120	180	240
7.94	13.13	385	146	37.8	28.0	16.9	7.9	3.5	2.3	1.9
6.80	12.73	358	126	43.0	32.3	19.1	8.9	3.9	2.8	2.1
5.67	15.33	438	410	47.7	34.6	20.3	9.0	4.0	2.6	2.2
4.53	14.32	414	603	44.7	33.3	18.8	8.3	3.7	2.3	1.8
3.40	14.38	429	302	50.1	38.6	20.1	8.7	3.9	2.7	1.9
2.27	10.88	329	120	46.0	34.0	17.8	7.4	3.1	1.8	1.4

a. Chemiluminescent reactions contained 0.10 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate(CPPO), 1.56 x 10^{-4} M sodium salicylate, 0.375 M H_2O_2 and the indicated concentrations of 1,8-dichloro-9,10-bis(phenylethynyl)anthracene (1,8-DCBPEA) in a solvent of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol.

b. Quantum yield in einsteins $mole^{-1}$.

c. Light capacity in lumen hours $liter^{-1}$.

d. Time (minutes) required for emission of 75% of the total amount of light.

confirmed this hypothesis.

A similar series of chemiluminescent reactions was carried out with 1,8-DCBPEA at 0.10 M CPPO (Table 4) and the highest light capacity (438 lumen hours liter^{-1}) was obtained at 5.67 x 10^{-3} M. The intensity values toward the end of the reactions do not appear to reflect any significant loss in fluorescer concentrations. This was also confirmed in the fluorescer decomposition studies (Section IV-F) where the decomposition rate of 1,8-DCBPEA was appreciably faster at 0.21 M CPPO than at 0.10 M CPPO.

C. The Effects of Additives in the Chemiluminescent Performance of 1,5- and 1,8-DCBPEA

A series of additives were evaluated with 0.21 M CPPO and 1,8-DCBPEA to investigate the relationship of additive structure to the reduction of concentration quenching. The results are summarized in Table 5. The highest light capacity (545 lumen hours liter^{-1}) was obtained with polyethylene oxide (Polyox WSRN-80). Other additives also improved performance but were generally less effective. The combination of Half-Second Butyrate and Polyox WSRN-80, which was previously found to be highly effective[3] with 1,5-DCBPEA, was somewhat less effective than Polyox alone. Half-Second Butyrate, alone, was substantially less effective.

A similar series (Table 6) was carried out using 1,5-DCBPEA as the fluorescer. In general, the performance of this fluorescer was poorer than the 1,8-isomer. Thus, without any additive, a light capacity of 410 lumen hours liter^{-1} was obtained with 1,8-DCBPEA in contrast with a value of 284 with 1,5-DCBPEA. A comparison of the intensity values at the 60 minute point and beyond indicates that fluorescer decomposition is contributing to the loss in efficiency with 1,5-DCBPEA. The highest value obtained with the 1,5-isomer was 360 lumen hours liter^{-1} as compared with 545 with 1,8-DCBPEA.

The improvement in performance using tetrabutylammonium perchlorate (TBAP) with 1,5-DCBPEA (Table 6) led us to examine this additive further with the 1,8-isomer. Substantial improvements in light output were found (maximum light capacity 620), as summarized in Table 7. Significant increases in light capacity were also obtained using combinations of Polyox WSRN-80 and a fluoro silicone. Performance data on systems containing Polyox WSRN-80 and TBAP with a series of catalyst concentrations are summarized in Table 8. Increasing the catalyst concentration has the anticipated effect of increasing brightness and shortening lifetime. The highest light capacity (683 lumen hours liter^{-1}) was obtained with TBAP although with a rather long lifetime (T.75 634 min.). The brightness after nearly eight hours (over two foot lamberts cm^{-1}) was particularly encouraging for a long-lived formulation.

The experiment with 2,4,6-tri-t-butylphenol (Table 7) was particularly interesting. This additive was found (Section IV-F) to substantially retard the decomposition rate of 1,8-DCBPEA. However, no significant increase in light capacity was observed when this free radical inhibitor was added to the CPPO - 1,8-DCBPEA reaction. Apparently the concentration of fluorescer (5.67 x 10^{-3} M) was sufficiently high to overcome any effect of fluorescer destruction on the light output. This experiment establishes that TBAP and the Polyox are increasing the light capacity by mechanisms other than fluorescer stabilization.

Polyethylene oxide was investigated further in a series of chemiluminescent experiments carried out on the 0.21 M CPPO - 1,8-DCBPEA formulation to determine the optimum concentration and the optimum molecular weight range of the polymer. Table 9 summarizes the effect of Polyox WSRN-80 concentration on chemiluminescent reactions containing 0.21 M CPPO. The maximum concentration of polymer employed in this series of experiments was 1% in the chemiluminescent reaction (1.3% in the oxalate component). Above this concentration of polymer the oxalate component becomes highly viscous and stirring the chemiluminescent reaction is difficult. No significant differences in performance were apparent between 0.3% and 1.0% concentrations (light capacities 598 and 597 respectively) but a slight loss in light capacity was observed at 0.1%. No large differences in lifetime were evident within the concentration range studied.

On the basis of these results, the effect of the polymer molecular weight was studied at two polymer concentrations (0.3% and 0.75%). The results summarized in Table 10 indicate a general trend of increasing light capacity with decreasing polymer molecular weight at the lower concentration. At the higher Polyox concentration the trend is less clear, but there is a significant decrease in light capacity with the 600,000 molecular weight range as compared to the lower polymers. The optimum range as determined from these experiments is the 400 molecular weight polymer.

The effect of a number of phenolic antioxidants on the performance of CPPO - 1,8-DCBPEA formulations was explored to determine the concentrations of these potential stabilizers which can be tolerated in the chemiluminescent reaction without seriously effecting the efficiency. Table 11 summarizes the effect of five known antioxidants on the chemiluminescent reaction. At 0.75×10^{-3} M and 3.75×10^{-3} M concentrations, 2,4,6-tri-t-butylphenol (TBP) had no significant effect on the light capacity or lifetime. No significant effect on performance was observed with 2,6-di-t-butyl-p-cresol (DBPC), but a 10% reduction in light capacity was found with 2,4-dimethyl-6-t-butylphenol (DMBP). The effect of the anisole derivatives, 3-t-butyl-4-hydroxyanisole (BHA) and 3,5-di-t-butyl-4-hydroxyanisole (DBHA), was more pronounced. Both of these compounds reduced the light capacity by more than 50% and increased the lifetime three fold. The reason the anisoles quench the chemiluminescent reaction is unclear at present, but cannot be due to an acidity effect since these compounds are weaker acids than the alkyl phenols.

The effect of a series of phenolic antioxidants on chemiluminescent reactions containing additives to reduce concentration quenching is summarized in Table 12. Only DBPC had any significant effect on reactions containing tetrabutylammonium perchlorate (TBAP) reducing the light capacity by 7%. The anisoles, BHA and DBHA, were used at one-fifth the concentration of the alkyl phenols because of the serious quenching problem observed in the reactions without any additive. In the reactions containing polyethylene oxide, only DBPC had a significant effect, reducing the light capacity by about 10%.

The data summarized in Table 13a illustrate the concentration quenching effects observed in the 1,8-DCBPEA - CPPO formulations. The additives, TBAP and Polyox 80, which give the greatest improvement in light capacity at 0.21 M CPPO are virtually without effect at 0.10 M CPPO. These additives must be increasing light output by reducing the chemical quenching effects at the high oxalate concentration.

The effect of the tetrafluoroborate salt was particularly interesting. A definite induction period was observed in the oxalate component used in the last four experiments either with no additive or with TBAP added. Addition of TBAFB caused this induction period to disappear. This TBAFB might be useful in protecting oxalate components aginst this undesirable effect. The tetrafluoroborate salt is equally as effective as the perchlorate salt in improving the light output with the additional benefit of reducing the lifetime.

Two lithium salts, the perchlorate and the trifluoroacetate, were evaluated in the CPPO-BPEA chemiluminescent system. The lithium salts were screened because lithium is known to react with carboxylic acids, which may be responsible for chemical quenching. In particular oxalic acid, a powerful quencher, has been identified in oxalate ester chemiluminescent reactions, and lithium oxalate is insoluble in organic solvents. Table 13a summarizes chemiluminescent experiments carried out by adding lithium trifluoroacetate and lithium perchlorate to the activator component. The two salts have opposite effects on the chemiluminescent reaction: lithium trifluoroacetate acts like a weakly basic catalyst increasing the early intensities and shortening the lifetime; the perchlorate salt tends to decrease the initial intensity and prolong the reaction. Both types of decay curve shapes can be useful depending upon the particular application.

The improvement in performance obtained by the addition of polyethylene

Table 5
Effect of Additives on Chemiluminescence Performance of 1,8-DCBPEA[a]

Additive[b]	Conc. (%)	Q. Y.[c] x 10^2	Lt. Cap.[d]	T 3/4[e]	Intensity (Ft. Lmbt. cm^{-1}) vs. Time							
					2	10	20	30	60	120	180	240
None		6.82	410	172	42.8	28.3	21.5	16.8	10.0	6.4	4.5	2.8
D.C. FS1265 10^3 cps grade	2.0	7.70	463	166	48.9	31.7	23.6	18.9	11.7	7.4	5.0	3.1
D.C. FS1265 300 cps grade	2.1	7.91	475	156	57.4	35.3	25.8	19.7	11.7	7.5	5.2	3.1
D.C. FS1265 10^4 cps grade	2.0	8.02	482	169	51.3	32.9	24.4	19.4	12.0	7.7	5.4	3.3
Polyox WSRN-80	0.3	9.07	545	235	54.8	28.3	20.9	17.8	12.8	8.6	6.4	4.5
Eastman Half-Second Butyrate	0.3	6.94	417	169	43.0	28.7	21.9	17.1	10.6	6.6	4.6	2.9
WSRN-80 + HSB	0.3 0.3	8.62	518	253	38.7	18.9	14.8	13.7	13.0	9.8	6.9	4.9

a. Chemiluminescent reaction contained 0.21 M CPPO, 0.375 M H_2O_2, 1.56 x 10^{-4} M sodium salicylate in a solvent of 75% dibutyl phthalate, 20% dimethyl phthalate and 5% t-butanol.

b. Polyox WSRN-80 is a polyethylene oxide from Union Carbide FS1265 is Dow Cornings Fluoro Silicone 1265 in the indicated viscosities. HSB is Eastman's Half-Second Butyrate, a cellulose acetate butyrate.

c. Quantum yield in einsteins $mole^{-1}$.

d. Light capacity in lumen hours $liter^{-1}$.

e. Time required for emission of 75% of the total amount of light.

Table 6

Effect of Additives on Chemiluminescence Performance of 1,5-DCBPEA[a]

Additives[b]							Intensity (Ft. Lmbt. cm^{-1}) vs. Time						
TBAP M x 10^2	WSRN-80 %	FS1265 %	HSB %	Q. Y.[c] x 10^2	Lt. Cap.[d]	T.75	2	10	30	60	120	180	240
---	---	---	---	4.23	284	74	48.2	32.0	16.5	8.2	3.3	1.4	0.5
3.7	---	---	---	5.34	357	164	33.6	23.5	15.2	9.9	5.6	3.7	2.4
---	0.3	---	---	4.96	332	127	46.2	25.1	14.7	9.7	5.1	3.1	1.8
---	---	2.0	---	4.64	311	73	53.2	34.6	18.0	9.1	3.7	1.5	0.5
---	---	---	0.3	4.50	301	73	50.9	33.5	17.7	9.0	3.5	1.5	0.5
3.7	0.3	---	---	5.38	360	122	48.0	29.8	17.6	10.5	5.1	2.9	1.6
---	0.3	---	0.3	4.89	328	148	37.5	19.2	12.1	9.8	6.1	3.6	2.0
---	0.3	2.0	0.3	5.21	349	151	43.4	21.0	12.7	10.1	6.4	3.8	2.1

a. Chemiluminescent reactions contained 0.21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate(CPPO), 1.35 x 10^{-3} M 1,5-dichloro-9,10-bis(phenylethynyl)anthracene(1,5-DCBPEA), 0.375 M H_2O_2 and 1.56 x 10^{-4} M sodium salicylate in a solution of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol.

b. TBAP is N,N,N,N-tetrabutylammonium perchlorate. Polyox WSRN-80 is a polyethylene oxide from Union Carbide. FS1265 is Dow Cornings Fluoro Silicone 1265; 10^4 cPs viscosity. HSB is Eastman's Half-second Butyrate, a cellulose acetate butyrate.

c. Quantum yield in einsteins $mole^{-1}$.

d. Light capacity in lumen hours $liter^{-1}$.

e. Time required for emission of 75% of the total amount of light.

Table 7

Effect of TBAP and Polyox on the Chemiluminescent Performance of 1,8-DCBPEA[a]

Additive[b]	Q. Y.[c] x 10^2	Lt. Cap.[d]	T.75[e]	Intensity (Ft. Lbt. cm^{-1}) vs. Time (min.)							
				2	10	30	60	120	180	240	480
None	7.11	427	180	46.7	29.4	17.1	9.6	6.0	4.2	3.1	0.6
3.7 x 10^{-2}M TBAP	10.00	601	272	52.4	22.7	16.0	14.0	9.7	6.5	5.0	1.7
7.5 x 10^{-2}M TBAP	9.96	598	285	50.0	26.7	18.2	12.9	8.5	6.1	4.6	2.1
3.7 x 10^{-3}M TBAP	10.32	620	259	40.0	27.8	18.4	13.9	9.7	7.0	5.2	1.7
7.5 x 10^{-3}M TBAP	10.22	614	232	40.3	27.0	19.3	15.0	10.3	7.1	5.1	1.5
0.3% Polyox WSRN-80 2% F.S.1265	10.23	615	286	51.8	31.1	19.0	12.6	8.6	6.7	4.9	2.1
0.3% Polyox WSRN-80 2% F.S. 1265 0.3% HSB	9.97	599	372	50.5	32.1	18.6	11.8	7.8	5.8	4.4	2.0

a. Chemiluminescent reactions contained 0.21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), 5.67 x 10^{-3} M 1,8-dichloro-9,10-bis(phenylethynyl)anthracene (1,8-DCBPEA), 0.375 M H_2O_2 and 1.56 x 10^{-4} M sodium salicylate in a solution of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol.

b. TBAP is N,N,N,N-tetrabutylammonium perchlorate. Polyox WSRN-80 is a polyethylene oxide from Union Carbide. FS 1265 is Dow Cornings Fluoro Silicone 1265, 10^4 cps viscosity. HSB is Eastman's Half-second Butyrate, a cellulose acetate butyrate.

c. Quantum yield in einsteins $mole^{-1}$.

d. Light capacity is lumen hours $liter^{-1}$.

e. Time required for emission of 75% of the total amount of light.

Table 8

Effect of Additives and Catalyst on the Chemiluminescent Performance of 1,8-DCBPEA[a]

TBAP M x 10^3	WSRN-80 %	NaSal M x 10^4	Q. Y.[b] x 10^2	Lt. Cap.[c] lm.hr.l.$^{-1}$	$T_{.75}$[d]	Intensity (Ft. Lbt. cm^{-1}) vs. Time							
						2	10	30	60	120	180	240	460
7.5	-----	1.56	11.37	683	634	44.9	28.7	17.2	11.2	7.7	5.8	3.8	2.3
7.5	-----	3.0	9.51	572	182	60.0	41.1	22.6	13.8	8.3	5.4	3.8	0.9
7.5	-----	5.0	9.94	597	103	93.4	57.3	29.3	16.5	7.0	3.3	2.0	0.5
---	0.3	1.56	9.44	567	516	47.3	22.6	13.8	10.0	7.3	5.5	4.7	2.1
---	0.3	3.0	9.97	599	285	53.3	28.7	18.5	13.5	9.0	6.3	4.7	1.6
---	0.3	5.0	9.14	549	148	62.2	33.6	24.1	15.9	9.0	5.3	3.2	0.5
7.5	0.3	3.0	9.62	578	107	77.1	45.3	28.2	18.2	9.5	4.5	2.2	0.1
---[e]	-----	3.0	6.97	419	204	37.5	27.3	16.4	9.3	6.0	4.2	3.3	0.9

a. Chemiluminescent reactions contained 0.21 M CPPO, 0.375 M H_2O_2, 5.67 x 10^{-3} M 1,8-DCBPEA and the indicated concentrations of tetrabutylammonium perchlorate (TBAP), Polyox WSRN-80 (a polyethylene oxide, m.w. 200,000) and sodium salicylate (NaSal). Solvent system was 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol.

b. TBAP is N,N,N,N-tetrabutylammonium perchlorate. Polyox WSRN-80 is a polyethylene oxide from Union Carbide. FS 1265 is Dow Cornings Fluoro Silicone 1265, 10^4 cps viscosity. HSB is Eastman's Half-Second Butyrate, a cellulose acetate butyrate.

c. Quantum yield in einsteins mole-1.

d. Light capacity in lumen hours liter-1.

e. This experiment contained 1 x 10^{-3} M 2,4,6-tri-t-butyl phenol.

Table 9

Effect of Polyox Concentration on Chemiluminescence Performance of 1,8-DCBPEA

Conc. Polyox WSRN-80[b]	Q. Y. x 10^2	Lt. Cap.	T.75	Intensity (Foot Lamberts cm^{-1}) vs. Time (Minutes)								
				2	10	30	60	90	120	180	240	420
0	7.10	427	181	46.8	30.0	17.5	10.3	8.0	6.3	4.5	3.3	.9
.1%	8.56	515	238	46.4	23.3	15.2	11.1	9.2	8.0	6.2	5.1	2.7
.3	9.97	599	271	58.3	29.2	18.2	12.6	9.8	8.3	6.3	5.1	2.7
.50	9.42	566	219	60.2	31.0	19.3	13.3	9.9	8.0	6.3	4.9	2.0
.75	10.15	610	221	70.7	36.3	21.1	13.3	10.3	8.0	6.1	4.6	2.0
.75	10.11	607	285	58.6	31.3	19.1	13.4	10.3	8.6	6.1	4.4	2.5
1.0	9.58	576	204	60.6	34.2	19.9	14.1	10.9	9.0	6.2	5.1	1.4
1.0	9.93	597	202	72.7	40.0	21.0	13.4	10.3	8.7	6.8	5.0	2.0

[a] Chemiluminescent reactions contained 5.67 x 10^{-3} M 1,9-dichloro-9,10-bis(phenylethynyl)anthracene (1,8-DCBPEA), 1.56 x 10^{-4} M sodium salicylate, 0.375 M H_2O_2 and 0.21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO) in a solution of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol. The oxalate component containing CPPO, 1,8-DCBPEA and the Polyox was heated at 80°C for 5 to 10 minutes to effect complete solution of the polymers.

[b] Polyox WSRN-80 is Union Carbide's polyethylene oxide (mol. wt. 300,000).

Table 10

Effect of Polyox[a] Mol. Wt. on Chemiluminescence Performance of 1,8-DCBPEA[b]

Polyox Mol. Wt. x 10^3	POlyox Conc. %	Q. Y. x 10^2	Lt. Cap.	T.75	2 min.	10 min.	30 min.	60 min.	90 min.	120 min.	180 min.	240 min.
1	.75	9.12	548	353	34.9	20.9	15.4	12.2	10.0	8.4	6.1	4.7
4	.75	9.47	569	292	37.1	21.8	16.1	13.3	11.4	9.7	6.8	5.0
6	.75	8.59	516	431	25.0	12.2	8.5	7.4	7.2	7.4	6.8	6.0
20	.75	8.62	518	310	30.4	17.2	12.9	11.0	9.8	8.5	6.2	4.8
100	.75	9.18	551	292	61.1	27.3	16.3	11.2	9.2	7.7	6.1	4.9
200	.75	9.28	558	240	49.9	28.7	16.7	12.7	9.7	8.0	6.0	5.1
300	.75	8.80	529	530	54.3	25.2	14.2	9.8	7.7	6.5	4.8	3.9
600	.75	7.40	444	399	46.0	21.2	11.9	7.6	6.2	5.3	4.4	3.7
1	.30	8.99	540	345	31.2	20.6	16.1	12.7	10.1	8.3	6.0	4.5
4	.30	8.98	540	225	36.6	23.4	17.8	13.6	10.9	9.0	6.3	4.6
6	.30	8.47	509	436	26.5	13.4	9.2	7.7	7.3	7.2	6.6	5.6
20	.30	7.17	431	398	23.0	11.7	8.3	6.8	6.2	5.8	5.1	4.3
100	.30	7.84	471	322	48.2	21.3	12.3	8.9	7.5	6.4	5.2	4.4
200	.30	7.51	452	272	43.5	22.0	12.9	9.4	7.5	6.3	4.7	3.7
300	.30	7.51	451	341	35.9	18.5	11.1	8.2	6.7	5.8	4.6	3.9
600	.30	7.72	464	355	38.6	18.4	11.4	8.3	6.7	5.9	4.7	4.0

a. Polyox is Union Carbide's polyoxyethylene glycol.

b. Chemiluminescent reactions contained 5.67 x 10^{-3} M 1,8-dichloro-9,10-bis(phenylethynyl)anthracene (1,8-DCBPEA), 1.56 x 10-4 M sodium salicylate, 0.375 M H_2O_2 and 0.21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO) in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol. The oxalate component containing CPPO, 1,8-DCBPEA and the Polyox was heated at 80°C for 5 to 10 minutes to effect complete solution of the polymers.

Table 11

Effect of Phenolic Antioxidants on Chemiluminescence Performance of CPPO - 1,8-DCBPEA Formulations[a]

Additive[b]	Additive[c] M x 10^3	NaSal[c] M x 10^4	Lt. Cap.[d]	Q. Y. X 10^2	T-75[e]	Intensity (Ft. Lmbt cm^{-1}) vs. Time (Min.)						
						2	10	30	60	120	180	240
None	----	3	477	7.94	90	74.7	44.2	23.5	13.2	6.4	3.4	1.7
TBP	.75	3	497	8.27	83	74.7	47.5	25.1	13.9	6.4	3.2	1.5
None	----	5	473	7.87	82	69.4	57.3	27.6	12.7	4.6	2.2	1.3
TBP	3.75	5	456	7.58	93	62.4	47.4	25.7	13.8	4.9	2.1	1.2
DBPC	3.75	5	464	7.73	100	55.2	42.2	27.1	14.6	4.9	2.2	1.3
DMBP	3.75	5	434	7.23	124	38.7	28.8	21.8	15.6	6.3	2.8	1.5
BHA	3.75	5	226	3.77	325	12.0	7.0	5.8	6.0	3.7	2.5	2.0
DBHA	3.75	5	228	3.80	342	11.6	5.2	4.1	4.6	3.5	2.7	2.4

a. Chemiluminescent reactions contained: 0.21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), 5.67 x 10^{-3} M 1,8-dichloro-9,10-bis(phenylethynyl)anthracene (1,8-DCBPEA), 0.375 M H_2O_2 and the indicated concentrations of sodium salicylate (NaSal) in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol.

b. Additives used 2,4,6-tri-t-butylphenol (TBP), 2,6-di-t-butyl-p-cresol (DBPC), 2,4-dimethyl-6-t-butylphenol (DMBP), 3-t-butyl-4-hydroxyanisole (BHA) and 3,5-di-t-butyl-4-hydroxyanisole (DBHA).

c. Concentrations in the chemiluminescent reaction.

d. Light capacity in lumen hours per liter.

e. Time required for emission of 75% of the total amount of light.

Table 12
Effect of Phenolic Antioxidants on Chemiluminescent Performance of Systems Containing Polyox, TBAP and TBAFB[a]

Phenol[b]	M x 10^3 [c]	Additive[b]	Conc.[c]	Lt. Cap.[d]	Q. Y. x 10^2	T-75[e]	Intensity (Ft. Lbt. cm^{-1}) vs. Time (Minute) 2	10	30	60	120	180	240
None	----	TBAP	.75 x 10^{-4} M	542	9.02	147	77.4	50.4	25.3	13.1	5.9	3.6	2.4
TBP	3.75	TBAP	.75 x 10^{-4} M	532	8.85	178	61.4	42.0	24.0	13.3	5.7	3.3	2.3
DBPC	3.75	TBAP	.75 x 10^{-4} M	502	8.36	185	63.7	45.5	25.1	12.3	4.5	2.6	2.0
BHA	.75	TBAP	.75 x 10^{-4} M	561	9.34	262	54.0	47.0	23.8	12.3	6.0	4.1	3.0
DBHA	.75	TBAP	.75 x 10^{-4} M	571	9.51	230	61.0	47.3	23.9	12.5	6.2	4.2	3.1
None	----	Polyox 80	.3%	548	9.10	139	59.0	35.6	25.9	16.6	8.6	4.9	2.8
DBPC	3.75	Polyox 80	.3%	493	8.21	124	43.2	27.6	23.2	17.4	9.0	4.1	2.3
BHA	.75	Polyox 80	.3%	555	9.23	167	32.5	24.1	21.9	17.7	10.4	6.5	3.8
DBHA	.75	Polyox 80	.3%	552	9.19	149	32.4	24.6	23.4	20.4	10.4	5.7	3.2
TBP	3.75	CW4M	.3%	525	8.74	311	42.7	28.4	19.9	13.3	7.3	4.5	3.2
DBPC	3.75	CW4M	.3%	502	8.35	202	42.6	28.3	19.9	13.7	7.2	4.2	3.0
TBP	3.75	TBAFB	.37 x 10^{-4} M	547	9.11	284	54.9	38.1	23.1	13.6	6.6	4.7	2.9

a. Chemiluminescent reactions contained: 0.21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), 5.67 x 10^{-3} M 1,8-dichloro-9,10-bis(phenylethynyl)anthracene (1,8-DCBPEA), 0.375 M H_2O_2 and 5.0 x 10-4 M sodium salicylate (NaSal) in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol.

b. Phenols used: 2,4,6-tri-t-butylphenol (TBP), 2,6-di-t-butyl-p-cresol (DBPC), 3-t-butyl-4-hydroxyanisole (BHA) and 3,5-di-t-butyl-4-hydroxyanisole (DBHA). Additives used: tetrabutylammonium perchlorate (TBAP), tetrabutylammonium tetrafluoroborate (TBAFB), Polyox WSRN-80 (polyethylene oxide, 300,000 mol. wt.) and Carbowax 4000 (polyethylene oxide 4000 mol. wt.)

c. Concentrations in the chemiluminescent reaction.

d. Light capacity in lumen hours per liter.

e. Time required for emission of 75% of the total amount of light.

Table 13

Effect of Additives of Concentration Quenching in the CPPO - 1,8-DCBPEA System[a]

Additive[b]	Conc.[c]	CPPO[c] M	NaSal[c] $\underline{M} \times 10^4$	Lt. Cap.[d]	Q. Y.	T.75[e]	Intensity (Ft. Lbt. cm^{-1}) vs. Time (Min.)						
							2	10	30	60	120	180	240
None	------	.10	1.56	438	15.33	410	47.7	34.6	20.3	9.0	4.0	2.6	2.2
None	------	.21	5.0	450	7.49	73	101.6	58.8	22.7	8.9	3.0	1.6	1.2
TBAP	$3.6 \times 10^{-3} \underline{M}$	.10	1.56	414	14.45	503	36.0	25.5	16.9	9.3	4.5	3.0	2.3
TBAP	$7.5 \times 10^{-3} \underline{M}$	.21	5.0	542	9.02	147	77.4	50.4	25.3	13.1	5.9	3.6	2.4
Polyox 80	.14%	.10	1.56	405	14.15	508	28.2	14.9	10.2	7.7	5.5	4.2	3.3
Polyox 80	.3 %	.21	5.0	548	9.10	139	59.0	35.6	25.9	16.6	8.6	4.9	2.8
None	------	.21	3.0	478	7.95	171	38.4	48.5	24.4	11.6	5.4	3.6	2.6
TBAP	$7.5 \times 10^{-3} \underline{M}$	.21	3.0	595	9.87	246	33.0	40.6	31.6	14.7	7.4	5.0	3.6
TBAFB	$7.5 \times 10^{-3} \underline{M}$	.21	3.0	605	10.05	145	55.6	38.9	29.0	18.7	9.4	4.3	2.8
TBAFB	$3.7 \times 10^{-3} \underline{M}$	.21	3.0	619	10.29	184	54.6	44.2	31.4	19.0	7.6	4.7	3.2

a. Chemiluminescent reactions contained: 5.67×10^{-3} $\underline{M}$ 1,8-dichloro-9,10-bis(phenylethynyl)anthracene (1,8-DCBPEA), 0.375 $\underline{M}$ H_2O_2 and the indicated amounts of bis(2,4,5-trichloro-6-carbopentoxyphenyl) oxalate (CPPO) and sodium salicylate (NaSal) in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol.

b. Additives used: tetrabutylammonium perchlorate (TBAP), tetrabutylammonium tetrafluoroborate (TBAFB) and Polyox WSRN-80 (polyethylene oxide, 300,000 mol. wt.).

c. Concentrations in the chemiluminescent reaction.

d. Light capacity in lumen hours per liter.

e. Time required for emission of 75% of the total amount of light.

Table 13a

Effect of Lithium Salts in CPPO Chemiluminescence[a]

	Additive[b]	CPPO Conc. M	Q. Y. Einst. $mol^{-1} \times 10^2$	Lf. Tm. T 3/4	Lt. Cap. ($lm.hr.l.^{-1}$)	Intensity ($ft. lbt. cm^{-1}$ vs Time) 2	10	30	60	90	120	180
Control	---	0.10	10.2	106	301	26.7	23.0	17.3	10.4	6.9	4.3	2.1
	.01 M LPC[c]	0.10				15.6	10.8	9.1	7.0	5.8	4.5	3.0
Control	---	0.10	10.0	91	296	27.4	23.8	18.9	11.1	6.5	3.8	2.0
	.01 M LTA	0.10	9.89	29	292	72.9	56.3	20.6	5.2	1.3	0.3	<0.1
Control	---	0.21	2.92	87	181	21.8	16.6	10.5	6.3	4.0	2.5	1.2
	.01 M LTA	0.21	3.38	19	209	80.3	48.6	9.1	1.6	0.5	0.2	<0.1

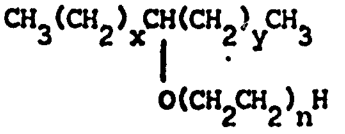
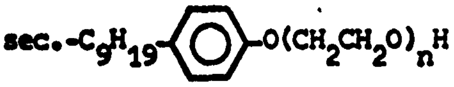
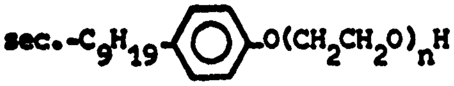
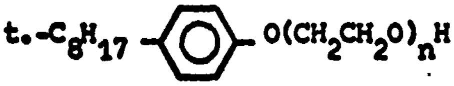
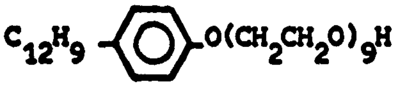
a. Chemiluminescent reactions contained the indicated concentration of bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), 2.25×10^{-3} M 9,10-bis(phenylethynyl)anthracene (BPEA), 1.6×10^{-4} M sodium salicylate and 0.375 M H_2O_2 in a solvent of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol.

b. Concentrations of anhydrous lithium perchlorate (LPC) and anhydrous lithium trifluoroacetate (LTA) in the chemiluminescent reaction. The lithium salts were dissolved in the activator component.

c. The lifetime of this reaction was too long for accurate determination of quantum yield and light capacity.

Table 13b

Screening of Additives for CPPO Chemiluminescence

Tergitol Nonionic 15-S-7	U. Carbide	 $CH_3(CH_2)_xCH(CH_2)_yCH_3$ with $O(CH_2CH_2)_nH$ $x + y = 9$ to 13 $n = 7$	Good
Flexol 3GO	U. Carbide	Triethylene glycol Di(2-ethyl)hexoate	Good
Flexol 3GH	U. Carbide	Triethylene glycol Di(2-ethylbutyrate)	Good
Dibutylcarbitol	U. Carbide	$C_4H_9(OCH_2CH_2)_2OC_4H_9$	Poor
Surfonic N-40	Jefferson		Poor
Igepal CO-530	G. A. F.		Poor
Igepal CA-620	G. A. F.		Poor
Tergitol Nonionic 12-P-7	U. Carbide		Poor

a. Standard CPPO oxalate component was diluted 2:1 with additive and compared visually against a control sample diluted with dibutyl phthalate in the chemiluminescent reaction with H_2O_2.

Table 13c

Effect of Additives in the Chemiluminescent Performance of CPPO[a]

Additive[b]	Concentration	Q. Y.[c] x 10^2	Lt. Cap.[d]	T.75	Intensity (ft. lbt. cm^{-1}) vs. Time (min)					
					2	10	30	60	120	180
None	---	11.53	299	73	30.9	29.0	21.4	10.3	2.9	1.3
Flexol 3GH	1%	11.06	286	71	31.6	28.6	20.8	9.8	2.7	1.2
	5%	10.78	279	72	29.9	28.3	20.3	9.3	2.7	1.2
	10%	11.90	308	77	30.7	31.0	21.8	10.1	3.0	1.4
Flexol 3GO	1%	11.04	286	70	32.1	28.3	20.8	9.9	2.7	1.2
	5%	11.12	288	71	31.5	27.8	21.2	9.9	2.8	1.2
Tergitol 15-s-7	1%	11.59	300	151	29.3	17.3	13.1	9.3	4.7	2.7
	5%	11.04	286	134	29.1	17.4	13.7	9.4	4.6	2.5

[a] Chemiluminescent reactions contained 0.375 M H_2O_2, 1.56 x 10^{-3} M sodium salicylate, 0.0878 M bis(2,4,5-trichloro-6-carbopentoxy)phenyl oxalate (CPPO) and 2.0 x 10^{-3} M 9,10-bis(phenylethynyl)anthracene (BPEA) in a solvent of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol.

[b] Flexol 3GH is triethylene glycol di(2-ethylbutrate); Flexol 3GO is triethylene glycol di(2-ethylhexoate); Tergitol 15-S-7 is a polyethylene glycol monoether. All these materials were obtained from Union Carbide. Concentration given in the chemiluminescent reaction.

[c] Quantum yield in einsteins $mole^{-1}$.

[d] Light capacity in lumen hours $liter^{-1}$.

[e] Time required for emission of 75% of the total light.

oxides prompted us to study the effect of a number of commercially available polyethylene glycol derivatives wherein one or both hydroxyl substitutents are blocked as ether or ester groups. Table 13b summarizes the results of qualitative screening tests designed to eliminate those materials which obviously quench the chemiluminescent reaction. The additives which performed "good" were evaluated quantitatively in the CPPO-BPEA system (Table 13c). The results indicate that none of these materials gave significant improvement over the control sample which contained no additive. The Tergitol 15-S-7 lengthened the lifetime appreciably but no improvement in light capacity was found.

D. Storage Stability of Formulations Containing 1,8-DCBPEA

Results from a series of accelerated storage stability experiments on 1,8-DCBPEA formulations are summarized in Table 14. In dibutyl phthalate solution 1,8-DCBPEA decomposes at a moderate rate in the dark at 75°C even in the absence of CPPO; 44% is lost in 21 days. Air does not effect this reaction. In the absence of air, CPPO has no effect. But in the presence of both air and CPPO, fluorescer decomposition is markedly accelerated. This latter rapid decomposition is substantially reduced by the addition of the antioxidant TBP. In contrast, TBP has little effect in the absence of air. In general, the loss of light capacity parallels the loss of fluorescer.

These results are consistent with a fluorescer decomposition mechanism involving two major pathways: (1) a thermal decomposition which takes place under all conditions at 75°C and (2) an autooxidation-derived, free radical induced decomposition, which is promoted by the presence of CPPO. The thermal process may be difficult to eliminate, but it is clearly possible to minimize the autooxidation process by adding a sufficient amount of an efficient free radical inhibitor which probably scavanges radicals produced from the decomposition of CPPO.

The products from the decomposition of 1,8-DCBPEA have not been isolated and identified. The absorption spectra of the oxalate components (Figure 2) indicate that a product with an absorption maximum near 465 nm is being formed at the expense of 1,8-DCBPEA. The chemiluminescent emission from samples containing large amounts of the decomposition products is shifted slightly towards the red (a yellow-orange color). Fluorescence measurements indicate that the fluorescence efficiency of the by-product is from 35 to 70% lower than 1,8-DCBPEA. However, the results in Table 15 indicate that the products from the decomposition have no large effect on the chemiluminescent efficiency, suggesting that the lowering of the fluorescer concentration is the major factor in the decrease in light capacity in samples stored at 75°C.

Results discussed earlier indicated that a substantial proportion of concentration quenching is observed at high CPPO concentrations with 1,8-DCBPEA in the absence of additives (typical values are light capacity 450 at 0.21 M CPPO and 438 at 0.10 M CPPO). Thus, small losses of CPPO in storage at 75°C should not be reflected in the light capacity. This has been verified experimentally from the results summarized in Table 16 by storage of an oxalate component containing CPPO alone in dibutyl phthalate. After 35 days at 75°C, 91% of the initial light capacity was retained. This compares with 16% of the initial light capacity left after 21 days from the sample stored with CPPO and 1,8-DCBPEA. A similar result was found when TBP was added to the CPPO solutions. These results support the conclusion that fluorescer decomposition is responsible for most of the decrease in light capacity of oxalate components containing 1,8-DCBPEA on storage at 75°C.

The additives which give the greatest improvement in light capacity (TBAP and the polyethylene oxides) tend to promote destruction of the fluorescer in storage tests as indicated by the results summarized in Table 17. The appearance of the intensity decay curves obtained from these stored solutions is similar to those obtained from the oxalates stored without additives.

The results summarized in Table 18 indicate that at .005 M additive concentration all three antioxidants increase the storage lifetime of the oxalate components containing 1,8-DCBPEA. Better performance was found with DBPC and

DMBP (58% and 54% of the initial light capacity retained after 35 days at 75°C) than with TBP (24% left after 35 days). The additives which reduce concentration quenching (TBAP, TBAFB and the polyethylene oxide) were found to deteriorate rapidly even in the presence of .005 M TBP.

A set of supplementary storage stability experiments have been completed at 50°C, and the results are summarized in Table 19. As expected, the rate of fluorescer decomposition and loss in light capacity is slower at this temperature. The absorption spectra are also similar, suggesting that the same product are being formed in both cases.

The use of an antioxidant such as TBP has been shown to retard the rate of fluorescer destruction in the presence of CPPO and air, as discussed earlier (Table 15), although the decomposition rate with .001 M TBP was still rapid. Thus, two other efficient antioxidants, 2,6-di-t-butyl cresol (DBPC) and 2,4-dimethyl-6-t-butylphenol (DMBP), were compared with TBP at .005 M concentration in an attempt to provide better storage lifetime for the oxalate components containing 1,8-DCBPEA. In addition, the effect of the higher concentration of TBP on the storage stability of high light capacity formulations containing TBAP, TBAFB and polyethylene oxide was studied.

Table 19 summarizes the effect of several phenolic antioxidants on the 50°C storage stability of oxalate components formulated with 1,8-DCBPEA. At .005 M concentration (in the oxalate component) the alkylated phenols 2,6-di-t-butyl-p-cresol (DBPC) and 2,4-dimethyl-6-t-butylphenol (DMBP) retarded the autooxidation of the fluorescer and gave acceptable storage stability after 116 days at 50°C. Only 10% of the initial light capacity was lost with DBPC added as an antioxidant and only 20% was lost with DMBP. The formulation containing Polyox WSRN-80 had slightly better storage stability than the formulation with tetrabutylammonium perchlorate (TBAP). The two anisoles, 2-t-butyl-4-hydroxyanisole (BHA) and 2,6-di-t-butyl-4-hydroxyanisole (DBHA), quenched the chemiluminescent reaction at 0.005 M in the oxalate component, but provided good storage stability for these low light capacity

Table 14

Decomposition of 1,8-DCBPEA[a] at 75°C

Oxalate Component[b]	Stored Under	Days at 75°	% 1,8-DCBPEA Remaining[c]	% of Initial Lt. Cap.	Lt. Cap.[e]	NaSal[d] M x 10^4	Q. Y. x 10^2	T.75[f]	Intensity (Ft. Lmbt. cm^{-1}) vs. Time (Min.) 2	10	30		120	180	240
No CPPO[g]	Air	0	--	--	---	---	----	----	----	----	----	----	----	----	----
		7	85	--	---	---	----	----	----	----	----	----	----	----	----
		14	68	--	---	---	----	----	----	----	----	----	----	----	----
		21	56	--	---	---	----	----	----	----	----	----	----	----	----
.28 M CPPO[g]	Air	0	--	--	477	3	7.94	90	74.7	44.2	23.5	13.2	6.4	3.4	1.7
		7	60	57	270	3	4.50	81	45.6	28.3	15.2	8.1	3.2	1.5	0.6
		14	35	27	127	3	2.14	63	23.1	14.9	7.9	4.0	1.2	0.4	0.2
		21	15[i]	16	65	3	1.09	34	19.6	10.8	3.8	1.3	0.2	0.1	----
.28 M CPPO[g] .001 M TBP	Air	0	--	--	497	3	8.27	83	74.7	47.5	25.1	13.9	6.4	3.2	1.5
		7	79	70	348	3	5.79	99	53.3	34.2	18.2	9.7	4.4	2.3	1.3
		14	56	45	222	3	3.73	82	33.3	22.4	12.0	7.2	2.8	1.2	0.5
		21	32	30	149	3	2.48	43	36.7	22.2	9.2	3.6	0.8	0.3	0.1
No CPPO[h]	Argon	0	--	--	---	---	----	----	----	----	----	----	----	----	----
		7	71	--	---	---	----	----	----	----	----	----	----	----	----
		14	68	--	---	---	----	----	----	----	----	----	----	----	----
		21	55	--	---	---	----	----	----	----	----	----	----	----	----
		28	49	--	---	---	----	----	----	----	----	----	----	----	----
		35	55	--	---	---	----	----	----	----	----	----	----	----	----
.28 M CPPO[h]	Argon	0	--	--	540	5	8.99	61	66.3	91.6	32.6	9.9	2.7	1.5	1.0
		7	76	75	404	5	6.33	65	83.9	51.5	22.5	9.3	2.7	1.3	0.8
		14	71	64	347	5	5.78	78	47.7	38.9	19.0	9.0	3.0	1.4	0.8
		28	56	51	278	5	4.62	54	67.9	37.2	15.5	6.5	2.1	0.9	0.5
		35	55	57	308	5	5.13	58	71.5	43.3	15.7	3.5	1.0	0.5	0.3
.28 M CPPO[h] .001 M TBP	Argon	0	--	--	519	5	8.64	58	48.0	88.6	34.0	10.8	2.9	1.6	1.1
		7	71	73	381	5	6.73	71	73.6	46.6	21.3	9.1	2.8	1.4	0.9
		14	71	46	241	5	4.02	60	36.8	29.9	14.4	6.6	2.0	0.8	0.4
		21	55	63	328	5	5.46	69	62.3	39.6	19.1	9.0	3.0	1.3	0.7
		28	56	62	322	5	5.36	52	80.7	45.0	17.7	7.2	2.2	0.9	0.5
		35	53	62	318	5	5.30	54	90.2	45.9	16.6	6.2	1.8	0.9	0.5
.28 M CPPO[h]	Air	0	--	--	495	5	8.24	54	51.4	87.0	31.8	10.0	2.7	1.6	1.1
		7	54	61	303	5	5.04	58	63.7	39.7	17.7	7.4	2.2	1.0	0.6
		14	54	78	385	5	6.41	74	54.2	43.8	21.3	10.0	3.2	1.5	0.8
		21	43	40	198	5	3.29	59	35.3	26.1	12.6	5.6	1.7	0.7	0.3
		28	42	36	178	5	2.96	51	41.7	25.3	10.2	4.1	1.2	0.5	0.3
		35	38	35	174	5	2.89	57	41.5	24.7	9.1	3.5	1.0	0.5	0.3

Footnotes for Table 14

a. Chemiluminescent reactions contained 5.67×10^{-3} $\underline{M}$ 1,8-dichloro-9,10-bis(phenylethynyl)anthracene (1,8-DCBPEA), .21 $\underline{M}$ bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), the indicated concentrations of sodium salicylate (NaSal) and 0.375 $\underline{M}$ H_2O_2 in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol.

b. Oxalate components contained 7.67×10^{-3} $\underline{M}$ 1,8-DCBPEA and the indicated concentrations of CPPO and 2,4,6-tri-t-butylphenol (TBP).

c. Determined from the absorption band at 495 nm.

d. Concentration in the chemiluminescent reaction.

e. Light capacity in lumen hours per liter.

f. Time required for emission of 75% of the total amount of light.

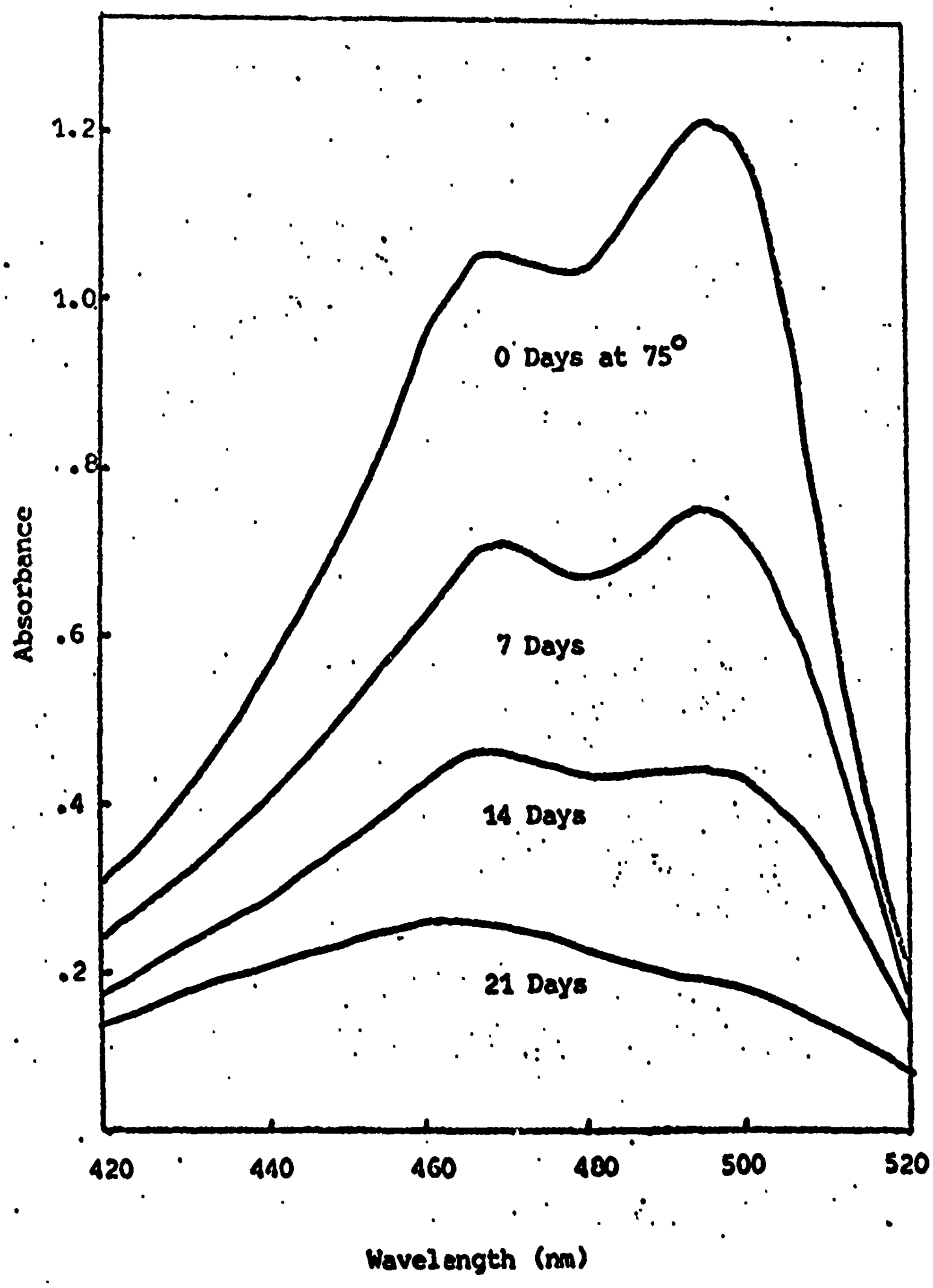
g. Stored in Teflon FEP bottles.

h. Stored in sealed N51A glass ampoules.

i. By-product absorption contributes to this value.

Figure 2

Absorption Spectra of Oxalate Components Containing 1,8-DCBPEA Stored at 75°C[a, b]



Footnotes for Figure 2

a. Oxalate components initially contained .28 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO) and 7.56×10^{-3} M 1,8-dichloro-9,10-bis(phenylethynyl)anthracene (1,8-DCBPEA) in dibutyl phthalate and were stored at 75°C in Teflon FEP bottles under air.

b. Absorption spectra were recorded on aliquots of the oxalate components diluted 1:200 with dibutyl phthalate.

Table 15

Effect of Fluorescer Decomposition Products on Chemiluminescence Efficiency of 1,8-DCBPEA

Oxalate Component[b]	Lt. Cap.[c]	Q. Y. x 10^2	T.75[d]	Intensity (Ft. Lbt. cm^{-1}) vs. Time (Min.) 2	10	30	60	90	120	180	240	366
.28 M CPPO 7.56 x 10^{-3} M 1,8-DCBPEA	297	4.95	326	22.2	15.3	8.1	5.2	4.2	3.8	3.2	2.7	1.7
.28 M CPPO 7.56 x 10^{-3} M 1,8-DCBPEA Fluorescer Decomposition Products from storage 35 days at 75°	268	4.46	219	23.6	17.3	10.8	6.6	4.7	3.9	2.9	2.1	0.9

a. Chemiluminescent reactions contained 0.21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), 5.67 x 10 M 1,8-dichloro-9,10-bis(phenylethynyl)anthracene (1,8-DCBPEA), 0.375 M H_2O_2 and 5 x 10^{-4} M sodium salicylate in a solvent of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol.

b. Oxalate components were not heat-treated.

c. Light capacity in lumen hours per liter.

d. Time required for emission of 75% of the total amount of light.

e. A solution of 7.56 x 10^{-3} M 1,8-DCBPEA in dibutyl phthalate was stored 35 days at 75° in Teflon FEP. Analysis indicated 55% of the original amount of fluorescer remained. Additional 1,8-DCBPEA and CPPO were added to adjust the concentrations to the indicated values.

Table 16

Storage Stabilities of CPPO 1,8-DCBPEA Formulations in Teflon FEP at 75°[a]

Stored CPPO Formulation	Days at 75°	% 1,8-DCBPEA[c] left	% of Initial Lt. Cap.	Lt. Cap.[d]	O. Y. x 10^2	T.75[e]	NaSal[f] M x 10^4	Intensity (Ft. Lbt. cm^{-1}) vs. Time (Min.) 2	10	30	60	120	180	240
.28 M CPPO 7.56 x 10^{-3} M 1,8-DCBPEA	0	---	---	477	7.94	90	3	74.7	44.2	23.5	13.2	6.4	3.4	1.7
	7	60	57	270	4.50	81	3	45.6	28.3	15.2	8.1	3.2	1.5	0.6
	14	35	27	127	2.14	63	3	23.1	14.9	7.9	4.0	1.2	0.4	0.2
	21	159	16	65	1.09	34	3	19.6	10.6	3.8	1.3	0.2	0.1	---
.25 M CPPO[b]	0	---	---	473	7.87	82	5	69.4	57.3	27.6	12.7	4.6	2.2	1.3
	7	---	93	437	7.27	65	5	101.0	57.7	22.3	8.7	2.9	1.6	1.0
	14	---	91	430	7.16	66	5	103.0	56.7	22.1	8.4	2.4	1.3	0.9
	21	---	90	427	7.10	65	5	108.0	54.7	21.0	8.8	2.9	1.5	1.0
	28	---	86	405	6.74	82	5	79.5	45.2	20.2	10.3	2.9	1.9	1.1
	35	---	91	427	7.11	72	5	99.8	52.8	20.8	9.1	3.3	1.3	1.1
.28 M CPPO 7.56 x 10^{-3} 1,8-DCBPEA .005 M TBP	0	---	---	456	7.58	93	5	62.4	47.4	25.7	13.8	4.9	2.1	1.2
	7	80	88	400	6.65	59	5	80.0	52.0	24.3	9.1	2.4	1.2	0.8
	14	58	66	297	4.94	56	5	59.1	40.1	18.6	6.4	1.7	0.8	0.5
	21	41	45	207	3.45	48	5	46.1	30.0	12.9	4.7	1.2	0.5	0.3
	28	29	33	149	2.48	64	5	25.4	18.0	9.3	4.3	1.2	0.4	0.2
	35	24	24	111	1.84	41	5	26.5	17.7	6.9	2.3	0.6	0.2	0.1
.28 M CPPO[b] .005 M TBP	0	---	---	372	6.20	122	5	25.5	36.5	20.3	11.0	5.1	2.3	1.6
	7	---	123	458	7.62	65	5	92.1	57.6	26.5	10.2	2.5	1.3	0.9
	14	---	128	475	7.91	87	5	92.1	56.4	26.3	9.8	2.4	1.3	0.3
	21	---	111	414	6.89	61	5	90.2	52.3	23.6	9.7	2.4	1.5	1.0
	28	---	112	415	6.90	94	5	68.0	42.6	21.5	11.7	4.2	1.9	1.1
	35	---	113	420	7.00	70	5	87.5	50.2	23.1	9.8	2.8	0.4	0.9

Footnotes for Table 16

a. Chemiluminescent reactions contained: .21 $\underline{M}$ bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), 5.67×10^{-3} $\underline{M}$ 1,8-dichloro-9,10-bis(phenylethynyl)anthracene (1,8-DCBPEA), the indicated concentration of sodium salicylate (NaSal) and 0.375 $\underline{M}$ H_2O_2 in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol.

b. These solutions were stored without fluorescer, aliquots were withdrawn at the appropriate time intervals and 1,8-DCBPEA added to the desired concentration, 7.56×10^{-3} $\underline{M}$.

c. Determined from absorption band at 495 nm.

d. Light capacity in lumen hours per liter.

e. Time required for emission of 75% of the total amount of light.

f. Concentration in the chemiluminescent reaction.

g. By-product absorption contributes to this value.

Table 17

Effect of Additives on the Storage Stability of Oxalate Components Containing 1,8-DCBPEA at 75° in Teflon FEP

Additive[b]	Days at 75°	% 1,8-DCBPEA Remaining[c]	Initial Lt. Cap.	Lt. Cap.[d]	Q. Y. x 10^2	T-75[e]	Intensity (Ft. Lbt. cm^{-1}) vs. Time (Minutes)						
							2	10	30	60	120	180	240
None	0	----	-----	477	7.94	90	74.7	44.2	23.5	13.2	6.4	3.4	1.7
	7	60	57	270	4.50	81	45.6	28.3	15.2	8.1	3.2	1.5	0.6
	14	35	27	127	2.14	63	23.1	14.9	7.9	4.0	1.2	0.4	0.2
	21	15[f]	16	65	1.09	34	19.6	10.8	3.8	1.3	0.2	0.1	---
0.01 M TBAP	0	----	-----	668	11.1	106	72.7	43.4	25.3	15.7	8.1	4.6	2.7
	7	46	38	251	4.18	101	36.0	23.4	13.0	7.3	3.2	1.7	0.9
	14	17[f]	10	70	1.17	74	12.0	7.5	4.0	2.2	0.7	0.3	0.1
	21	9[f]	4	36	0.60	47	8.5	4.8	2.3	0.9	0.2	0.1	---
0.4% Polyox WSRN-80	0	----	-----	599	9.96	164	56.8	28.3	18.0	13.6	8.5	5.8	4.1
	7	48	45	266	4.43	178	21.9	12.6	9.6	7.9	5.0	3.2	2.0
	14	22[f]	17	104	1.73	110	15.1	8.3	4.9	3.2	1.5	0.8	0.4
	21	9[f]	6	38	0.62	62	6.2	4.0	2.5	1.3	0.3	0.1	0.1

a. Chemiluminescent reactions contained 0.21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), 5.67×10^{-3} M 1,8-dichloro-9,10-bis(phenylethynyl)anthracene, (1,8-DCBPEA), 0.375 M H_2O_2 and 3×10^{-4} M sodium salicylate in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol.

b. Concentration in the oxalate component. Additives used: tetrabutylammonium perchlorate (TBAP) and Polyox WSRN-80 (polyethylene oxide 300,000 mol. wt.).

c. Determined from the absorption band at 495 nm.

d. Light capacity in lumen hours per liter.

e. Time required for emission of 75% of the total amount of light.

f. By-product absorption contributes to this value.

Table 18

Effect of Phenolic Antioxidants in the Storage Stability of Oxalate Components Containing 1,8-DCBPEA at 75°

Phenol^b	M x 10^3	Additive^c	Conc.	Days Stored at 75°	% 1,8-DCBPEA Left^d	% of Initial Lt. Cap.	Lt. Cap.^{e}	Q. Y. x 10^2	T.75^f	Intensity (Ft. Lbt. cm^{-1})Vs. Time (Min.)						
										2	10	30	60	120	180	240
TBP	5	None	-----	0	----	--	456	7.58	93	62.4	47.4	25.7	13.8	4.9	2.1	1.2
				7	80	88	400	6.66	59	80.0	52.0	24.3	9.1	2.4	1.2	0.8
				14	58	66	297	4.94	56	59.1	40.1	18.6	6.4	1.7	0.8	0.5
				21	41	45	207	3.45	48	46.1	30.0	12.9	4.7	1.2	0.5	0.3
				28	33	33	149	2.48	64	25.4	18.0	9.3	4.3	1.2	0.4	0.3
				35	24	24	111	1.84	41	26.5	17.7	6.9	2.3	0.6	0.2	0.2
DBPC	5	None	-----	0	----	--	464	7.73	100	55.2	42.2	27.1	14.6	4.9	2.2	1.3
				7	79	93	433	7.21	57	80.3	58.0	28.0	9.8	2.6	1.2	0.8
				14	65	78	364	6.06	57	68.7	49.2	23.2	7.7	2.0	1.0	0.6
				21	49	70	327	5.44	51	68.0	46.9	19.9	7.2	1.9	0.9	0.5
				28	48	60	277	4.61	68	44.5	32.3	17.4	8.0	2.3	0.9	0.5
				35	40	58	267	4.44	48	55.3	39.7	16.4	5.9	1.6	0.7	0.4
DMBP	5	None	-----	0	----	--	434	7.23	124	36.7	28.8	21.8	15.6	6.3	2.8	1.5
				7	82	91	396	6.59	66	53.3	42.8	28.7	12.1	3.0	1.3	0.7
				14	68	79	344	5.72	61	49.3	39.4	25.9	9.6	2.3	1.0	0.6
				21	53	73	318	5.29	65	46.6	36.7	22.0	8.7	2.2	0.9	0.5
				28	53	60	261	4.35	78	31.1	23.9	17.5	9.1	2.6	1.0	0.5
				35	39	64	233	3.89	55	37.2	30.7	16.2	6.2	1.7	0.7	0.3
TBP	5	CW4M	.4%	0	----	--	525	8.74	311	42.7	28.4	19.9	13.3	7.3	4.5	3.2
				7	77	80	429	7.15	219	40.5	27.3	17.5	11.0	5.8	3.5	2.4
				14	54	52	275	4.57	147	27.2	18.7	12.4	8.1	4.1	2.4	1.4
				21	37	35	184	3.06	128	18.5	12.7	8.6	5.9	3.0	1.6	0.9
				28	26	25	129	2.13	107	11.0	7.7	6.1	4.8	2.2	0.9	0.5
				35	19^g	16	84	1.40	85	9.7	7.1	5.1	3.1	1.2	0.5	0.2
TBP	5	TBAP	.01 M	0	----	--	532	8.85	178	61.4	42.0	24.0	13.3	5.7	3.3	2.3
				7	70	69	365	6.07	80	60.0	40.4	21.2	9.7	3.4	1.7	1.0
				14	48	42	223	3.72	62	37.7	26.9	14.5	7.2	1.8	0.8	0.4
				21	25^g	25	131	2.19	60	23.7	15.9	8.5	3.8	1.1	0.4	0.2
				28	23^g	16	86	1.42	74	12.2	8.4	5.4	3.0	0.9	0.3	0.1
				35	14	10	52	0.87	53	9.3	6.6	3.6	1.5	0.4	0.1	---
TBF	5	TBAFB	.005 M	0	----	--	547	9.11	284	54.9	38.1	23.1	13.6	6.6	4.7	2.9
				7	77	72	399	6.64	91	56.6	40.8	22.1	11.7	4.7	2.3	1.2
				14	55	72	399	6.64	74	38.0	29.8	17.0	8.2	2.8	1.3	0.6
				21	33	30	168	2.79	66	25.0	18.9	10.9	5.4	1.6	0.6	0.3
				28	27	20	109	1.81	77	12.9	10.0	7.0	4.1	1.2	0.4	0.2
				35	17^g	13	70	1.16	55	10.9	8.5	5.1	2.2	0.5	0.2	0.1

Footnotes for Table 18

a. Chemiluminescent reactions contained 0.21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl) oxalate (CPPO), 5.67 x 10^{-3} M 1,8-dichloro-9,10-bis(pentylethynyl)anthracene (1,8-DCBPEA), 0.375 M H_2O_2, 5 x 10^{-4} M sodium salicylate in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol. Oxalate components contained 0.28 M CPPO and 7.56 x 10^{-3} M 1,8-DCBPEA stored in Teflon FEP bottles.

b. Phenols used: 2,4,6-tri-t-butylphenol (TBP), 2,6-di-t-butyl-p-cresol (DBPC) and 2,4-dimethyl-6-t-butylphenol(DMBP). Concentrations are in the oxalate component.

c. Additives used: Tetrabutylammonium perchlorate (TBAP), Carbowax 4000, a polyethylene oxide 4000 mol. wt. (CW4M) and tetrabutylammonium tetrafluoroborate (TBAFB). Concentrations are in the oxalate component.

d. Determined from absorption band at 495 nm.

e. Light capacity in lumen hours per liter.

f. Time required for emission of 75% of the total amount of light.

g. By-product absorption contributes to this value.

Table 19

Effect of Phenolic Antioxidants on the Storage Stability of Oxalate Components Containing 1,8-DCBPEA at 50°a,b

Antioxidant[c]	M x 10^3	Additive[d]	Conc.	Days at 50°	% 1,8-DCBPEA Remaining	% of Initial Lt. Cap.	Lt. Cap.	Q. Y. x 10^2	T.75	Intensity (Ft. Lbt. cm^{-1}) Vs. Time (Minutes)							
										2	10	30	60	90	120	180	240
None	-	None	-----	0	--	---	450	7.49	73	100.6	58.8	22.7	8.9	4.6	3.0	1.6	1.2
				7	91	88	396	6.59	77	74.7	46.1	21.4	10.2	5.7	3.5	1.7	1.0
				21	74	80	361	5.98	55	80.3	47.0	19.9	8.6	4.7	2.9	1.3	0.7
				35	--	83	372	6.19	59	86.4	49.9	20.2	7.9	4.1	2.5	1.2	0.7
				60	44	65	293	4.88	49	75.2	41.7	16.2	6.3	3.2	1.9	0.8	0.5
				116	29	38	169	2.81	32	53.8	28.1	9.6	3.1	1.4	0.7	0.2	0.1
DBPC	5	None	-----	0	--	---	441	7.33	77	70.5	49.7	27.6	10.9	4.8	2.7	1.3	1.0
				7	88	97	426	7.09	91	58.2	40.1	24.4	13.0	7.2	4.4	1.9	1.2
				21	90	94	414	6.89	83	65.2	41.9	24.4	11.8	6.3	3.7	1.7	1.0
				35	--	104	457	7.60	74	81.0	54.0	29.4	11.8	5.5	3.1	1.5	1.0
				60	72	106	466	7.76	69	82.1	54.0	28.5	11.8	5.7	3.2	1.5	1.0
				116	58	90	396	6.60	65	75.7	48.1	24.4	9.4	4.5	2.7	1.3	0.8
DMBP	5	None	-----	0	--	---	454	7.57	101	53.4	38.4	28.1	14.5	6.5	3.3	1.4	0.9
				7	94	87	399	6.64	113	42.2	28.4	20.6	14.3	8.7	5.5	2.5	1.3
				21	90	89	403	6.71	89	48.8	33.0	24.2	14.7	8.4	4.9	2.0	1.0
				35	--	96	437	7.28	75	60.3	42.4	30.0	15.5	7.0	3.7	1.6	0.9
				60	70	95	429	7.14	76	58.5	40.4	27.7	14.4	7.0	3.8	1.6	0.9
				116	58	80	364	6.06	66	37.9	37.9	25.1	11.0	5.2	2.9	1.2	0.7
DBPC	5	Polyox	.4%	0	--	---	493	8.21	124	43.2	27.6	23.2	17.4	13.0	9.0	4.1	2.3
				7	--	98	482	8.02	28	30.2	16.6	18.8	12.9	10.8	9.0	6.2	3.9
				21	93	95	467	7.78	144	41.9	25.2	20.3	14.4	11.2	8.5	4.6	2.6
				35	--	97	477	7.94	150	46.3	29.0	23.4	16.2	11.5	8.0	3.9	2.1
				60	75	100	494	8.22	142	43.7	27.4	22.0	15.8	11.8	8.9	4.8	2.7
				116	70	83	409	6.81	134	37.4	23.8	18.8	13.3	9.8	7.3	3.8	2.1
DBPC	5	TBAP	.01 M	0	--	---	502	8.36	185	63.1	45.5	25.1	12.3	6.9	4.5	2.6	2.0
				7	93	98	493	8.20	195	52.8	36.0	21.9	13.4	8.5	5.7	3.2	2.1
				21	89	96	480	8.00	124	60.3	40.1	24.0	13.7	8.6	5.7	3.1	2.0
				35	--	97	486	8.09	98	68.0	47.2	27.2	13.6	7.7	5.0	2.7	1.7
				60	71	93	468	7.80	94	69.2	45.6	26.0	13.5	7.7	4.9	2.5	1.5
				116	64	75	378	6.28	74	62.4	40.2	22.6	11.1	6.0	3.7	1.7	0.9
DBPC	5	CW4M	.4%	0	--	---	502	8.35	202	42.6	28.3	19.9	13.7	9.8	7.2	4.8	8.0
				7	84	93	466	7.76	259	34.2	22.6	18.8	11.0	8.8	8.9	4.5	3.0
				21	89	85	429	7.14	173	37.0	24.1	17.6	13.1	8.9	6.8	4.2	2.7
				35	--	90	451	7.50	150	42.3	29.3	20.8	14.3	9.0	6.6	3.8	2.4
				60	70	88	443	7.37	177	41.9	26.9	19.4	12.3	8.7	6.6	4.0	2.6
				116	64	70	354	5.89	138	35.3	22.7	16.4	11.6	7.2	5.3	3.0	1.8
BHA	5	None	-----	0	--	---	226	3.77	325	12.0	7.0	5.8	6.0	4.7	3.7	2.5	2.0
				7	97	103	235	3.91	356	10.0	5.7	5.2	6.2	5.2	4.1	2.7	1.8
				21	97	97	220	3.66	270	11.4	6.4	5.5	6.0	5.2	4.1	2.7	1.9
				35	--	109	246	4.10	277	13.8	7.8	6.8	6.8	5.3	4.1	2.7	2.0
				60	78	107	243	4.05	319	14.8	8.2	6.6	6.2	4.8	3.8	2.5	1.8
				116	66	85	192	3.20	282	13.1	7.0	5.4	4.7	3.6	2.9	2.0	1.4
DBHA	5	None	-----	0	--	---	228	3.80	432	11.6	5.2	4.1	4.6	4.1	3.5	2.7	2.4
				7	98	95	216	3.60	380	9.8	4.5	3.6	4.5	3.9	3.4	2.6	2.0
				21	96	102	232	3.86	397	11.8	5.0	4.2	4.8	4.2	3.6	2.7	2.1
				35	--	99	226	3.76	321	13.4	5.7	4.8	5.1	4.3	3.5	2.7	2.1
				60	83	110	250	4.16	431	15.5	6.7	5.2	5.0	4.1	3.5	2.7	2.2
				116	66	105	240	3.99	323	17.9	9.1	7.2	5.1	3.8	3.1	2.2	1.7
BHA	1	None	-----	0	--	---	489	8.14	63	109.0	64.3	26.6	11.0	5.9	3.8	1.9	1.1
				7	81	78	387	6.45	109	57.7	39.2	18.9	10.1	6.9	5.1	2.8	1.7
				21	58	63	308	5.14	82	47.8	32.2	17.3	9.6	5.9	3.7	1.7	0.7
				42	20	20	97	1.62	44	21.2	13.6	6.8	2.6	1.0	0.5	0.1	---
				62	5	5	24	0.41	45	5.1	3.5	1.7	0.6	0.2	0.1	---	---
				90	--	2	11	0.19	34	[illegible]	1.8	0.8	[illegible]	0.1	---	----	---
DBHA	1	None	-----	0	--	---	473	7.87	69	103.	61.1	25.5	10.3	5.8	3.7	[illegible]	[illegible]
				7	73	86	406	6.76	104	63.9	47.0	20.0	[illegible]	6.9	[illegible]	[illegible]	[illegible]
				21	38	17	225	3.74	54	42.0	29.1	14.9	[illegible]	3.4	[illegible]	0.5	[illegible]
				42	15	14	67	1.11	33	19.0	11.3	4.5	1.3	[illegible]	[illegible]	[illegible]	---
				62	5	5	26	0.41	57	1.6	3.0	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	---
				90	--	2	11	0.10	52	2.1	1.4	[illegible]	[illegible]	[illegible]	---	---	---

Footnotes for Table 19

a. Chemiluminescent reactions contained 0.21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), .375 M H_2O_2, 5 x 10^{-4} M sodium salicylate and 5.67 x 10^{-3} M 1,8-dichloro-9,10-bis(phenylethynyl) anthracene (1,8-DCBPEA) in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate and 5% t-butanol.

b. Oxalate components contained 0.28 M CPPO, 7.56 x 10^{-7} M 1,8-DCBPEA and the indicated concentrations of antioxidants and additives stored in Teflon FEP bottles at 75°.

c. Antioxidants used: 2,6-di-t-butyl-p-cresol (DBPC), 2,4-dimethyl-6-t-butylphenol (DMBP), 2-t-butyl-4-hydroxyanisole (BHA) and 2,6-di-t-butyl-4-hydroxyanisole. Concentration is in the oxalate components.

d. Additives used: polyethylene oxide 300,000 mol. wt. (Polyox WSRN-80), polyethylene oxide 4,000 mol. wt. (CW4M) and tetrabutyl ammonium perchlorate (TBAP).

formulations. Reducing the concentrations of BHA and DBHA to .001 M overcame the quenching problem, but storage stability was much poorer.

Table 20 summarizes additional storage stability experiments designed to explore the effect of different solvents, dimethyl phthalate (DMP) and dibutyl terephthalate (DBTP) and the effect of sodium salicylate on the storage lifetime of oxalate components containing 1,8-DCBPEA. None of these formulations showed any improvement compared to the standard 1,8-DCBPEA.oxalate component. The rapid failure in DBTP indicated an impurity might be present in this solvent.

The storage stabilities of oxalate components containing 0.133 M CPPO and 7.56 x 10^{-3} M 1,8-DCBPEA at 75°C is summarized in Table 21. In the absence of antioxidant, the 0.133 M formulation is more storage stable than the analogous 0.28 M CPPO oxalate component (Table 17). Again, the use of an antioxidant such as DBPC retards the destruction of the fluorescer and improves the storage lifetime. The anisoles, BHA and DBHA, were less effective than the alkyl phenols as antioxidants for these formulations.

E. Relative Storage Stabilities of Oxalate Components Containing Different Fluorescers

A series of storage stability experiments were carried out on oxalate components containing 0.28 M CPPO and four different fluorescers: BPEA, 1-ClBPEA, 1,5-DCBPEA and 2-ClBPEA. The relative storage stability of these formulations was determined under a standard set of conditions to assess the relationship between fluorescer structure and stability and thus facilitate the design of more stable oxalate components. The results summarized in Table 22 indicate the relative order of fluorescer stability is: BPEA $>$ 1-ClBPEA $\cong$ 2-ClBPEA $\gg$ 1,5-DCBPEA. A comparison with earlier results on similar oxalates containing 1,8-DCBPEA indicates this fluorescer is somewhat less stable than the 1,5-isomer. These results are in general agreement with molecular orbital calculations carried out by Dr. M. Orloff in another program.[9] The loss in light capacity generally parallels the decrease in fluorescer concentration. It appears evident that the rate of fluorescer

Table 20

Storage Stabilities of 1,8-DCBPEA Oxalate Components Containing .28 M CPPO at 75°[a]

Oxalate Component[b]	Solvent	Days at 75°	% Flr. Remaining	% Initial Lt. Cap.	Lt. Cap.	Q. Y. x.10^2	T·75	Intensity (Ft. Lmbt. cm^{-1}) vs. Time (Minutes) 2	10	30	60	90	120	180	240
1,8-DCBPEA	DBP	0	--	--	480	7.99	--	117.5	68.1	25.3	10.5	5.6	3.3	1.7	1.0
		7	67	77	372	6.19	52	83.4	53.4	21.7	9.0	4.6	2.7	1.2	---
		14	53	65	312	5.18	44	74.7	47.2	19.0	7.4	3.5	1.9	0.6	0.2
		28	42	46	220	3.66	36	43.6	23.1	7.9	2.4	0.9	0.4	0.1	0.1
1,8-DCBPEA 1.5 x 10^{-4} M NaSal	DBP	0	--	--	466	7.76	55	115.6	66.2	24.0	9.8	5.1	3.1	1.5	0.9
		7	58	67	310	5.16	49	52.2	43.9	18.2	7.5	3.8	2.1	0.9	---
		14	37	49	229	3.81	40	58.7	35.6	14.3	4.9	2.1	1.1	0.4	0.2
		28	26	30	138	2.29	32	43.6	23.1	7.9	2.4	0.9	0.4	0.1	0.1
1,8-DCBPEA	DMP	0	--	--	463	7.71	60	86.1	62.7	27.4	12.7	6.7	3.7	1.5	0.7
		7	60	65	301	5.00	44	53.2	42.2	23.4	8.6	3.5	1.6	0.4	---
		14	36	44	204	3.40	37	44.6	32.5	15.5	4.5	1.4	0.5	0.1	0.1
		28	27	25	118	1.96	29	34.1	21.2	7.7	1.8	0.5	0.2	0.1	---
1,8-DCBPEA	DBTP	0	--	--	460	7.65	80	79.1	61.7	24.7	11.0	6.4	4.1	2.3	1.5
		7	86	2	7.1	0.1	157	----	----	0.1	0.1	0.2	0.3	0.4	---

a. Chemiluminescent reactions contained .21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate, 5.67 x 10^{-3} M 1,8-dichloro-9,10-bis(phenylethynyl)-anthracene (1,8-DCBPEA), .375 M H_2O_2 and 5 x 10^{-4} M sodium salicylate. Solvent mixture used: 20% dimethyl phthalate (DMP), 5% t-butanol and 75% of the solvent indicated; dibutyl phthalate (DBP), dibutyl terephthalate (DBTP) or DMP.

b. Oxalate components were stored in Teflon FEP bottles and contained .28 M CPPO and 5.67 x 10^{3} M 1,8-DCBPEA in the indicated solvent.

Table 21

Storage Stabilities of 1,8-DCBPEA Oxalate Components Containing .133 M CPPO at $75^{\circ a,b}$

Antioxidant	Days at 75°	% 1,8-DCBPEA Remaining	% of Initial Lt. Cap.	Lt. Cap.	Q. Y. x 10^2	T·75	Intensity (Ft. Lmbts. cm^{-1}) vs. Time (Min.)						
							2	10	30	60	90	120	180
None	0	---	---	304	10.6	91	53.1	35.7	17.6	5.6	2.9	2.0	1.4
	7	66	103	314	11.0	161	53.8	37.2	15.2	5.0	2.7	1.9	1.2
	21	46	83	253	8.64	171	37.3	26.9	12.3	4.9	2.6	1.7	1.0
	42	25	46	139	4.87	76	24.8	16.9	7.8	3.2	1.7	1.1	0.6
	62	17	29	87	3.03	86	13.6	8.4	4.8	2.6	1.5	1.0	0.5
	90	---	11	34	1.20	70	6.1	3.6	2.0	1.0	0.6	0.4	0.1
TBP	0	---	---	296	10.4	70	53.2	37.7	18.6	5.2	2.5	1.7	1.2
	7	73	109	324	11.3	92	61.7	44.4	17.2	4.8	2.3	1.5	1.0
	21	60	99	294	10.3	173	47.1	32.3	14.5	5.1	2.6	1.7	1.1
	42	41	72	212	7.40	84	37.4	25.4	11.5	4.4	2.4	1.6	1.0
	62	32	52	153	5.35	182	21.3	12.6	6.2	3.2	2.1	1.6	1.1
	90	---	38	114	3.97	148	14.9	9.0	5.1	2.8	1.8	1.4	0.9
DBPC	0	---	---	316	11.1	62	56.4	40.6	20.4	5.9	2.8	1.9	1.4
	7	76	116	358	12.5	126	64.6	47.6	18.3	5.2	2.6	1.8	1.2
	21	64	94	298	10.4	17	51.0	35.2	15.6	5.4	2.7	1.7	1.1
	42	41	72	227	7.94	95	40.4	26.4	12.1	4.7	2.4	1.6	1.0
	62	37	52	166	5.81	185	23.5	13.8	6.9	3.4	2.3	1.7	1.2
	90	---	40	125	4.36	159	12.4	8.1	4.8	2.8	1.7	1.2	0.6
DMBP	0	---	---	299	10.5	67	51.8	37.7	10.4	5.6	2.7	1.8	1.3
	7	78	112	334	11.7	83	62.6	46.6	17.5	5.0	2.4	1.6	1.1
	21	58	105	314	11.0	237	51.7	36.7	15.7	5.4	2.6	1.7	1.0
	42	40	68	202	7.07	75	37.4	25.0	11.2	4.4	2.3	1.5	.09
	62	30	44	131	4.59	142	18.8	11.8	5.9	3.0	2.0	1.5	1.0
	90	---	32	96	3.37	81	8.5	5.6	3.2	1.8	1.1	0.7	0.3
DBHA	0	---	---	214	7.47	151	27.9	20.0	11.7	4.5	2.8	2.1	1.5
	7	79	164	351	12.3		51.6	37.8	15.6	4.7	2.7	1.9	1.3
	21	68	141	302	10.6		47.5	32.9	14.6	5.4	2.8	1.8	1.1
	42	36	91	194	6.77	82	34.3	22.8	10.9	4.3	2.3	1.5	0.9
	62	27	70	149	5.21	160	18.2	12.5	6.9	3.5	2.3	1.7	1.1
	90	---	27	58	2.01	142	10.3	6.6	4.2	2.7	1.7	1.2	0.7
BHA	0	---	---	214	7.49	165	27.5	20.2	12.4	4.5	2.6	1.9	1.4
	7	79	136	291	10.2	----	38.3	33.2	14.5	4.3	2.2	1.6	1.2
	21	66	138	295	10.3	----	43.1	30.5	14.1	5.2	2.5	1.7	1.1
	42	43	91	195	6.82	81	35.2	22.7	10.8	4.4	2.3	1.5	0.9
	62	35	72	155	5.42	195	19.1	12.1	6.3	3.4	2.2	1.7	1.2
	90	---	43	92	3.23	34	2.8	1.8	0.8	0.2	0.1	---	---

Footnotes for Table 21

a. Chemiluminescent reactions contained .10 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate, 5.67×10^{-3} M 1,8-dichloro-9,10-bis(phenylethynyl)anthracene (1,8-DCBPEA), .375 M H_2O_2 and 1.56×10^{-4} M sodium salicylate in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate and 5% t-butanol.

b. Oxalate components were stored in Teflon FEP bottles and contained .133 M CPPO, 7.56×10^{-3} M 1,8-DCBPEA and the indicated concentration of 2,4,6-tri-t-butylphenol (TBP), 2,6-di-t-butyl-p-cresol (DBPC), 2,4-dimethyl-6-t-butylphenol (DMBP), 2,6-di-t-butyl-4-hydroxyanisole (DBHA) and 2-t-butyl-4-hydroxyanisole.

Table 22

Storage Stabilities of Various Fluorescers with .28 M CPPO at 75°[a]

Fluorescer	Conc. M x 10^3	Days Stored	% Flr. Remaining	% of Initial Lt. Cap.	Lt. Cap.	Q. Y. x 10^2	T-75	Intensity (Ft. Lmbt. cm^{-1}) vs. Time (Minutes)							
								2	10	30	60	90	120	180	240
BPEA	2.25	0	---	---	248	3.91	36	56.3	43.7	16.3	4.9	2.0	1.0	0.4	---
		7	95	99	246	3.87	43	63.6	35.2	15.9	5.8	2.4	1.2	0.4	0.1
		21	83	104	258	4.06	45	52.5	38.5	17.3	6.0	2.5	1.2	0.5	0.2
		28	92	96	239	3.76	41	50.8	38.2	16.1	5.3	2.3	1.2	0.5	---
		42	99	94	233	3.66	62	52.5	38.1	15.6	5.4	2.1	1.1	0.4	0.2
		49	93	90	222	3.50	39	48.6	36.7	15.0	4.5	1.8	0.9	0.3	0.2
		62	95	112	280	4.41	112	49.6	35.9	14.7	4.9	2.0	1.0	0.4	---
1-Cl BPEA	3.75	0	---	---	616	9.50	55	100.1	83.6	38.9	16.6	8.1	4.6	1.9	1.0
		7	100	113	701	10.8	70	113.7	74.8	40.2	20.2	10.9	6.2	2.7	1.0
		21	90	104	639	9.87	68	90.8	71.7	37.0	18.1	9.7	5.6	2.3	1.3
		28	---	105	651	10.1	67	91.3	76.9	38.8	18.4	10.1	6.1	2.7	1.4
		42	88	96	595	9.19	65	89.1	71.2	35.0	17.2	8.9	5.2	2.2	1.1
		49	81	93	571	8.82	62	80.4	69.6	35.4	16.3	8.4	4.7	1.9	0.9
		62	75	89	551	8.51	66	75.2	64.6	32.1	15.5	8.4	5.0	2.2	1.0
2-Cl BPEA	3.75	0	---	---	491	7.76	68	69.7	51.8	24.0	10.9	5.8	3.5	1.6	---
		7	100	107	525	8.30	86	76.7	44.5	23.9	12.8	7.2	4.3	1.9	1.0
		21	96	113	555	8.78	90	70.3	49.2	25.9	13.1	7.4	4.5	2.0	1.2
		28	97	103	504	7.97	81	64.6	48.0	24.3	12.3	7.2	4.5	2.1	---
		42	100	97	478	7.56	74	65.6	47.0	23.0	11.8	6.4	3.9	1.8	1.0
		49	93	96	473	7.47	75	61.5	45.5	23.0	11.4	6.3	3.8	1.7	0.9
		62	63	88	430	6.80	71	57.9	41.9	21.1	10.8	6.2	3.9	1.9	---
1,5-DCBPEA	1.13	0	---	---	221	3.31	25	81.6	42.8	11.2	3.1	1.2	0.5	0.2	---
		7	85	96	212	3.17	28	86.5	33.3	11.3	3.5	1.3	0.6	0.2	0.1
		21	68	81	179	2.67	27	65.9	31.6	9.5	2.5	0.9	0.4	0.1	0.1
		28	61	71	156	2.33	23	61.1	30.0	7.7	1.8	0.6	0.3	0.1	---
		42	43	45	99	1.49	19	47.4	18.6	4.2	0.9	0.3	0.1	---	---
		49	33	33	74	1.10	17	35.3	14.8	2.8	0.5	0.2	0.1	---	---
		62	22	20	45	0.68	17	23.2	8.5	1.6	0.3	0.1	0.1	---	---

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[a] Chemiluminescent reactions contained 0.21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), 0.375 M H_2O_2, 5 x 10^{-4} M sodium salicylate and the indicated concentrations of the following fluorescers: 9,10-bis(phenylethynyl) anthracene (BPEA), 1-chloro-9,10-bis(phenylethynyl)anthracene (1-Cl BPEA), 2-chloro-9,10-bis(phenylethynyl)anthracene (2-Cl BPEA) and 1,5-dichloro-9,10-bis(phenylethynyl)anthracene (1,5-DCBPEA).

decomposition in oxalate components at 75°C increases with the number of chlorine substituents on the anthracene nucleus. From a performance-stability viewpoint, 1-ClBPEA is the best fluorescer of those evaluated so far. The concentration of 1-ClBPEA employed in this set of experiments is not the optimum which was subsequently determined in a more extensive evaluation of this fluorescer (see Section IV-V). The low concentration of 1,5-DCBPEA used in those experiments was dictated by its low solubility in dibutyl phthalate.

F. Fluorescer Decomposition in the Chemiluminescent Reaction

The chemiluminescent performance results (Section IV-A) with 1,8-DCBPEA and BPEA indicated decomposition of the fluorescer might be contributing to the loss in efficiency of the chemiluminescent process at high CPPO concentrations, particularly during the later stages of the reaction. A method was therefore developed to monitor the concentration of fluorescer as a function of time during the chemiluminescent reaction. Table 23 summarizes the kinetic data on the fluorescer decomposition studies. With one exception (1-ClBPEA), the rates of decomposition of several fluorescers were found to follow a pseudo first order relation at 0.21 M CPPO (graphical data is presented in Appendix I), but deviated substantially from first order at 0.10 M CPPO. The data indicate that at 0.21 M CPPO 1,5-DCBPEA decomposes at a faster rate than either BPEA or 1,8-DCBPEA. This result coupled with the lower solubility of 1,5-DCBPEA would seem to rule out this fluorescer for consideration in a high light capacity system, especially since the concentration of this fluorescer cannot be increased enough to "swamp out" the decomposition effect. Chemiluminescent experiments at the solubility limit of 1,5-DCBPEA (Section IV-A) have confirmed this conclusion.

The addition of polyethylene oxide (WSRN-80) decreased the decomposition rate of 1,8-DCBPEA by more than half, suggesting that this additive was improving the light output by stabilizing the fluorescer. Similar effects were found with tetrabutylammonium perchlorate (TBAP) and 2,4,5-tri-butylphenol.

Table 23

Kinetics of Fluorescer Decomposition in the Chemiluminescent Reaction at 25°C[a]

Fluorescer	Initial Flr. Conc. M x 10^3	CPPO M	T 1/2[b]	-k[c] x 10^4	Relative Decomp. Rate
BPEA	2.25	0.10	31[d]	----------	----
BPEA	2.25	0.21	56[e]	2.26±.17[e]	1.00
1,8-DCBPEA	3.43	0.10	58[d]	----------	----
1,8-DCBPEA	3.43	0.21	39[e]	3.02±.20[e]	1.34
1,8-DCBPEA + 0.3% WSRN-80	3.43	0.21	87[e]	1.3 ±.17[e]	0.60
1,8-DCBPEA + 7.5 x 10^{-3} M TBAP	3.43	0.21	71[d]	1.60[f]	0.71
1,8-DCBPEA + 1 x 10^{-3} M TBP	3.43	0.21	77[d]	1.28[f]	0.57
1,5-DCBPEA	1.35	0.21	30[e]	3.82±.41[e]	1.68
1-ClBPEA	8.0	0.21	53[d]	g	----

[a] Chemiluminescent reactions contained the indicated concentrations of bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO) and fluorescer along with 0.375 M H_2O_2 and 1.56 x 10^{-4} M sodium salicylate in a solvent of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol. The 1-ClBPEA reaction contained 5 x 10^{-4} M sodium salicylate.

[b] Half-life (minutes) of the fluorescer in the chemiluminescent reaction.

[c] Pseudo first order rate constant (in second^{-1}) for the fluorescer decomposition.

[d] Estimated from absorbance versus time curve.

[e] Determined from least squares fit.

[f] Determined from graphical plot.

[g] Did not fit pseudo first order plot.

These results clearly establish that fluorescer destruction can contribute substantially to the loss in chemiluminescence efficiency at high CPPO concentration. Fortunately, this lowering in fluorescer concentration can be overcome by increasing the concentration of the fluorescer and/ or by use of an additive to minimize fluorescer destruction. The antioxidant, TBP, in addition to retarding the rate of fluorescer destruction is beneficial in improving the storage stability.

As more soluble oxalates are developed, and oxalate concentration increases fluorescer decomposition is expected to become more serious (1,8-DCBPEA decomposes faster at 0.21 M CPPO than at 0.10 M). The future development of high light capacity systems could depend on a fundamental knowledge of fluorescer decomposition mechanisms. The most likely fluorescer decomposition pathways are outlined in Chart III.

Chart III

Fluorescer Decomposition Pathways

$$(\text{Fluorescer} \cdot C_2O_4) \longrightarrow \text{Fluorescer Decomposition} \qquad (1)$$

$$\text{Fluorescer}^{*} \longrightarrow \text{Fluorescer Decomposition} \qquad (2)$$

$$\text{Fluorescer} + X \longrightarrow \text{Fluorescer Decomposition} \qquad (3)$$

Fluorescer destruction can arise from (1) a side reaction of the decomposition of the energy-rich complex of dioxetanedione and fluorescer, (2) a photodecomposition derived from the excited fluorescer or (3) a second (or higher) order chemical process with some other specie(s) in the ground state. We plan to continue efforts to determine which of these is responsible for fluorescer destruction since this knowledge is fundamental in designing higher light capacity systems.

[illegible]. Fluorescence of 1-ClBPEA and 2-ClBPEA

Two new fluorescers, 1-ClBPEA and 2-ClBPEA were prepared as described above in Section IV-A in attempts to incorporate the stability of BPEA and the desirable properties of 1,8-DCBPEA (resistance to fluorescence quenching by CPPO and high efficiency in the chemiluminescent system) into a single molecule. The fluorescence spectra of 1-ClBPEA and 2-ClBPEA are shown in Figure 3. The two fluorescence spectra are quite similar in shape, but the emission from 1-ClBPEA is shifted by about 20 nm towards longer wavelength and is visibly more yellow than the color of 2-ClBPEA fluorescence.

The extent of fluorescence quenching by CPPO on these two fluorescers was measured in two Stern Volmer[10] experiments which are summarized in Table 24. Both of these chloro derivatives have lower fluorescence quantum yields than BPEA (0.85) under similar conditions and are quenched by CPPO. The extent of this fluorescence quenching as compared to BPEA and 1,8-DCBPEA is illustrated in Figure 4. The relative magnitude of the slopes, a measure of the extent of fluorescence quenching by the oxalate ester, indicates that increasing chlorine substitution on the anthracene nucleus of BPEA reduces the extent of fluorescence quenching by CPPO. Thus, BPEA is the most severely quenched (slope 3.40), 1,8-DCBPEA is not quenched to any significant extent, and the mono-chloro derivatives fall between these two extremes (1-Cl slope 1.04, 2-Cl slope 1.43).

The presence of CPPO has very little effect on the fluorescence spectrum of either 1-ClBPEA (Figures 5a and 5b) or 2-ClBPEA (Figure 6). However, when the solvent mixture (75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol) used in the chemiluminescent reaction was employed for fluorescence measurements, higher fluorescence quantum yields were noted for 1-ClBPEA than were obtained in dibutyl phthalate alone (Table 25).

H. Spectral Changes in the Chemiluminescent Reaction

The effect of CPPO concentration on the spectral distribution of the emission from chemiluminescent reactions containing 2-ClBPEA is illustrated in Figure 7a. The general shape of the spectra at .10 M and .21 M CPPO is the same

Table 24

Effect of CPPO Concentration on the Fluorescence Quantum Yields of 1-Cl and 2-ClBPEA[a]

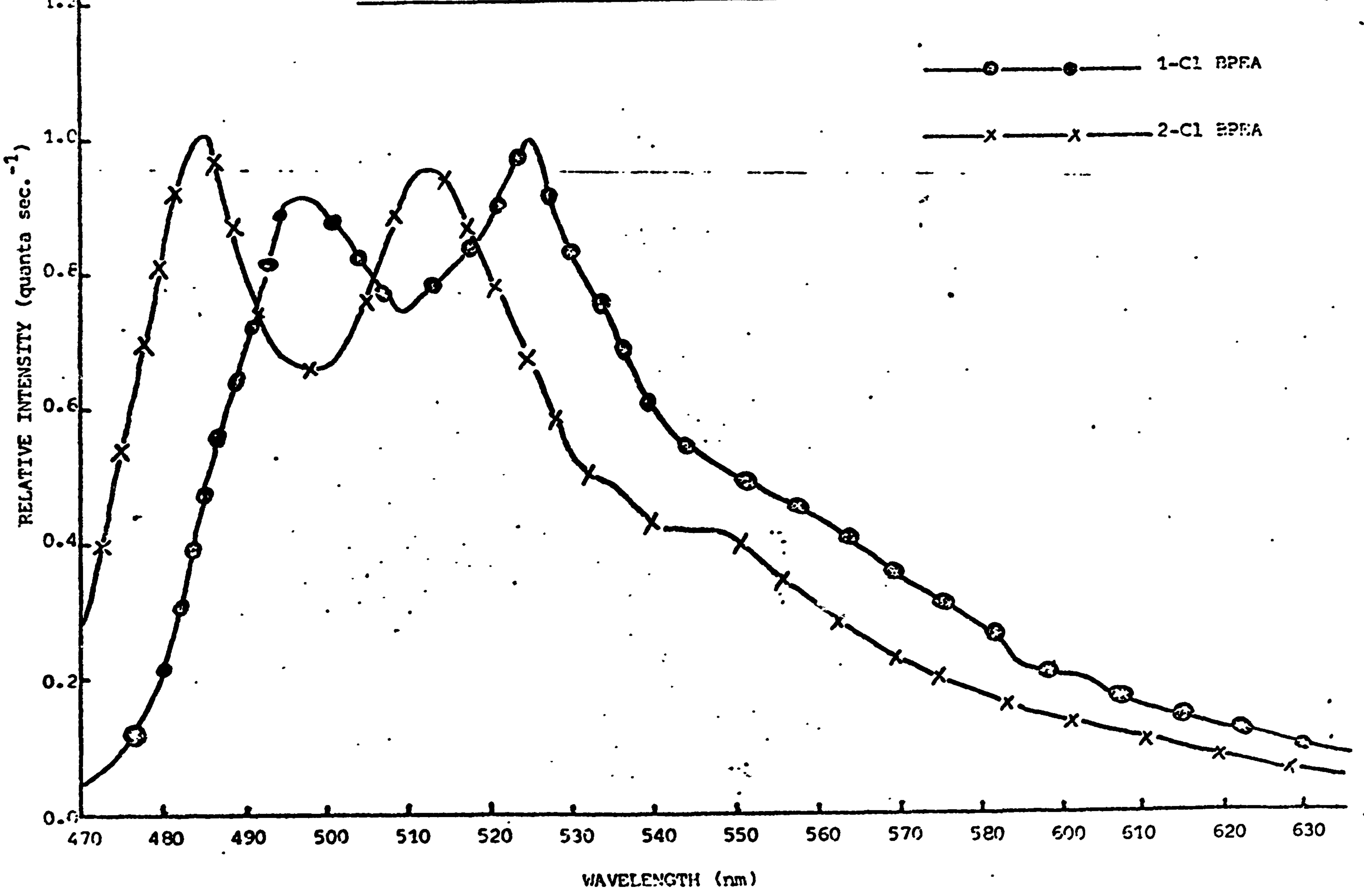
Conc. CPPO M	Fluorescence Quantum Yield[b]	
	1-ClBPEA	2-ClBPEA
0	0.710	0.665
0.07	0.664	0.593
0.14	0.626	0.552
0.21	0.584	0.511
0.28	0.527	0.482

[a] Concentration of 1-ClBPEA and 2-ClBPEA was 0.003 M in dibutyl phthalate.

[b] Excitation wavelength was 429 nm.

Figure 3

FLUORESCENCE SPECTRA OF MONO CHLORO BPEA DERIVATIVES



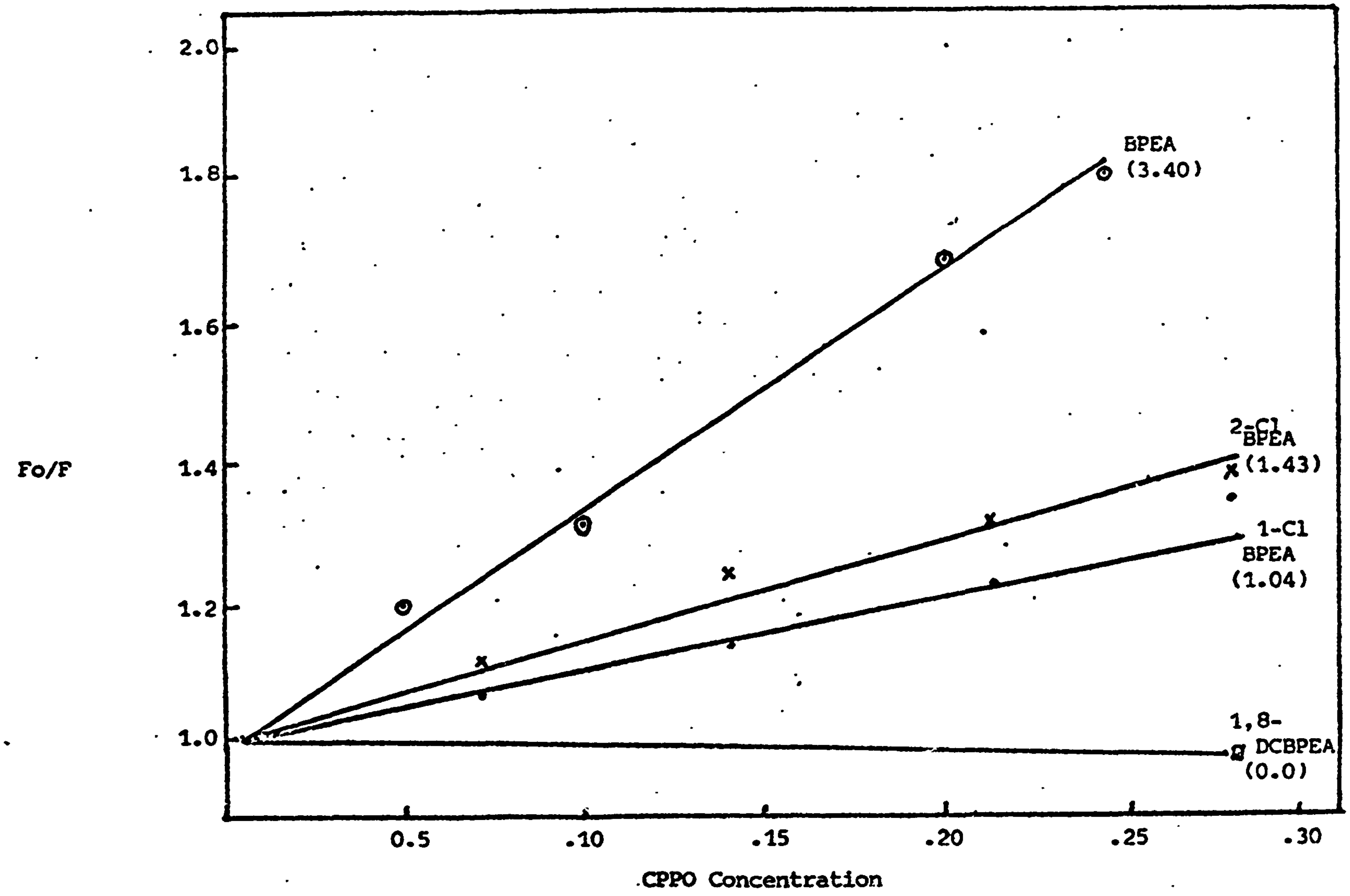
Footnotes to Figure 3

a. Concentration of 1-chloro-9,10-bis(phenylethynyl)anthracene (1-Cl BPEA) and 2-chloro-9,10-bis(phenylethynyl)anthracene (2-Cl BPEA) was 0.003 M in dibutyl phthalate.

b. Excitation wavelength was 429 nm.

Figure 4

CPPO QUENCHING OF FLUORESCENCE OF BPEA DERIVATIVES[a,b]



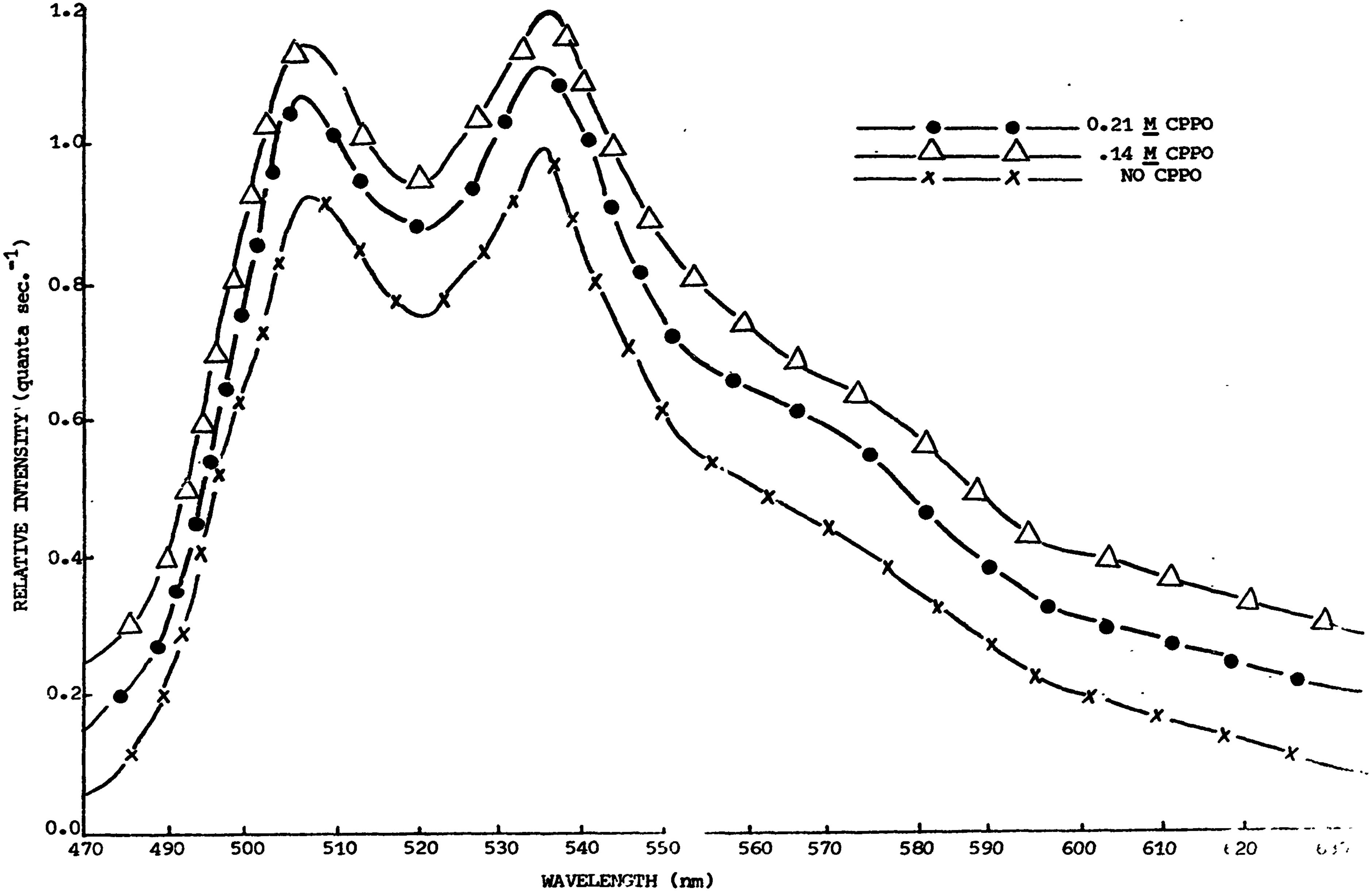
Footnotes to Figure 4

a. Concentrations of fluorescers were: 9,10-bis(phenylethynyl) anthracene (BPEA), 0.002 M; 1-chloro-9,10-bis(phenylethynyl) anthracene (1-Cl BPEA), .003 M; 2-chloro-9,10-bis(phenylethynyl)anthracene (2-Cl BPEA), .003 M; 1,8-dichloro-9,10-bis(phenylethynyl)anthracene (1,8-DCBPEA), .0045 M. Solvent was dibutyl phthalate. CPPO is bis (2,4,5-trichloro-6-carbopentoxyphenyl)oxalate. Slopes are indicated in parentheses.

b. Excitation wavelength was 429 nm.

Figure 5a

EFFECT OF CPPO CONCENTRATION ON FLUORESCENCE SPECTRUM OF 1-ClBPEA IN DIBUTYL PHTHALATE^a

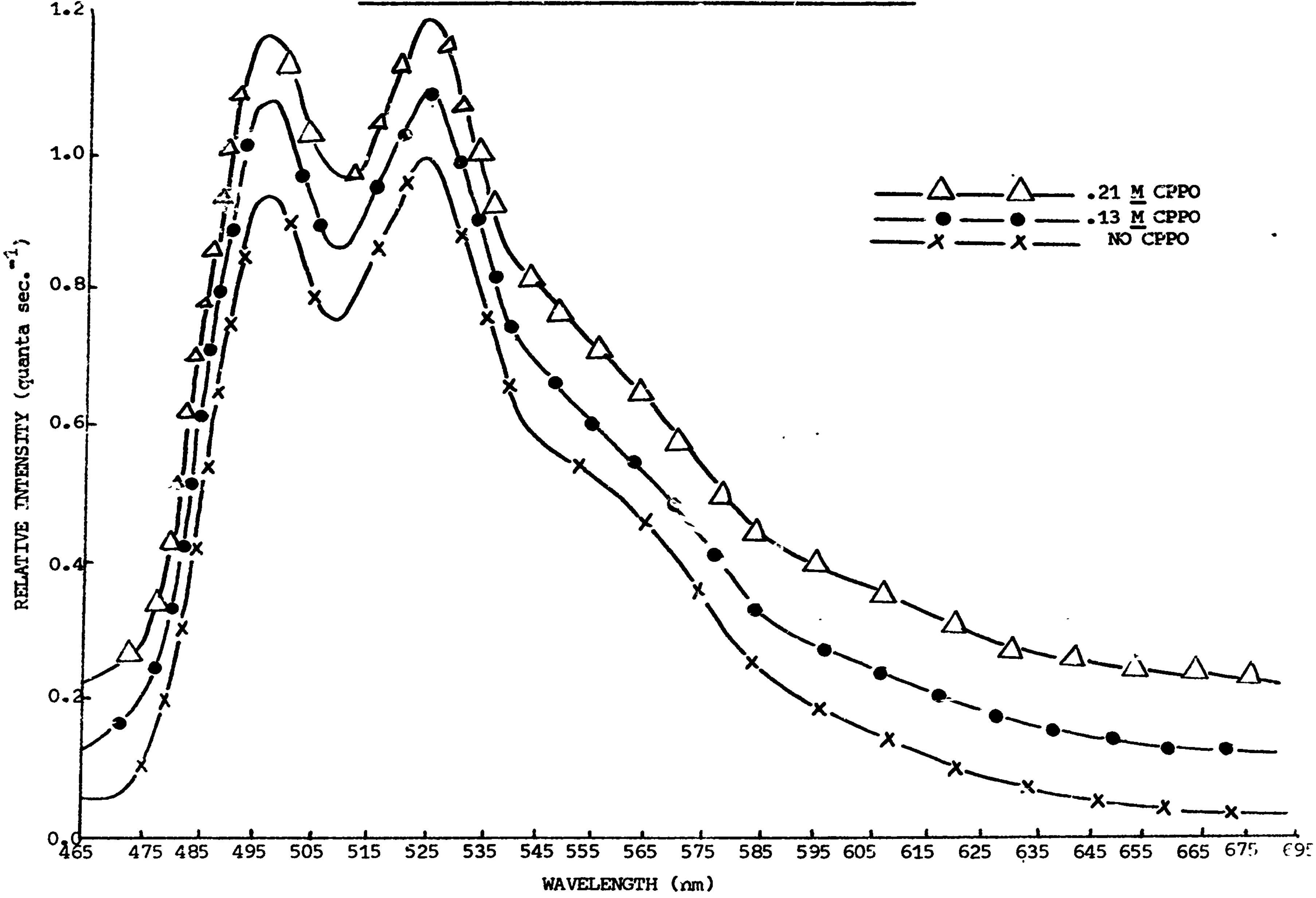


Footnotes to Figure 5a

a. Fluorescence spectra were measured on solutions containing .003 M 1-chloro-9,10-bis(phenylethynyl)anthracene (1-Cl BPEA) and the indicated concentrations of bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO) in dibutyl phthalate. Excitation wavelength was 429 nm. The two upper spectra have been displaced by increments of 0.1 along the ordinate.

Figure 5b

EFFECT OF CPPO CONCENTRATION ON FLUORESCENCE SPECTRUM OF 1-ClBPEA IN REACTION SOLVENT MIXTURE

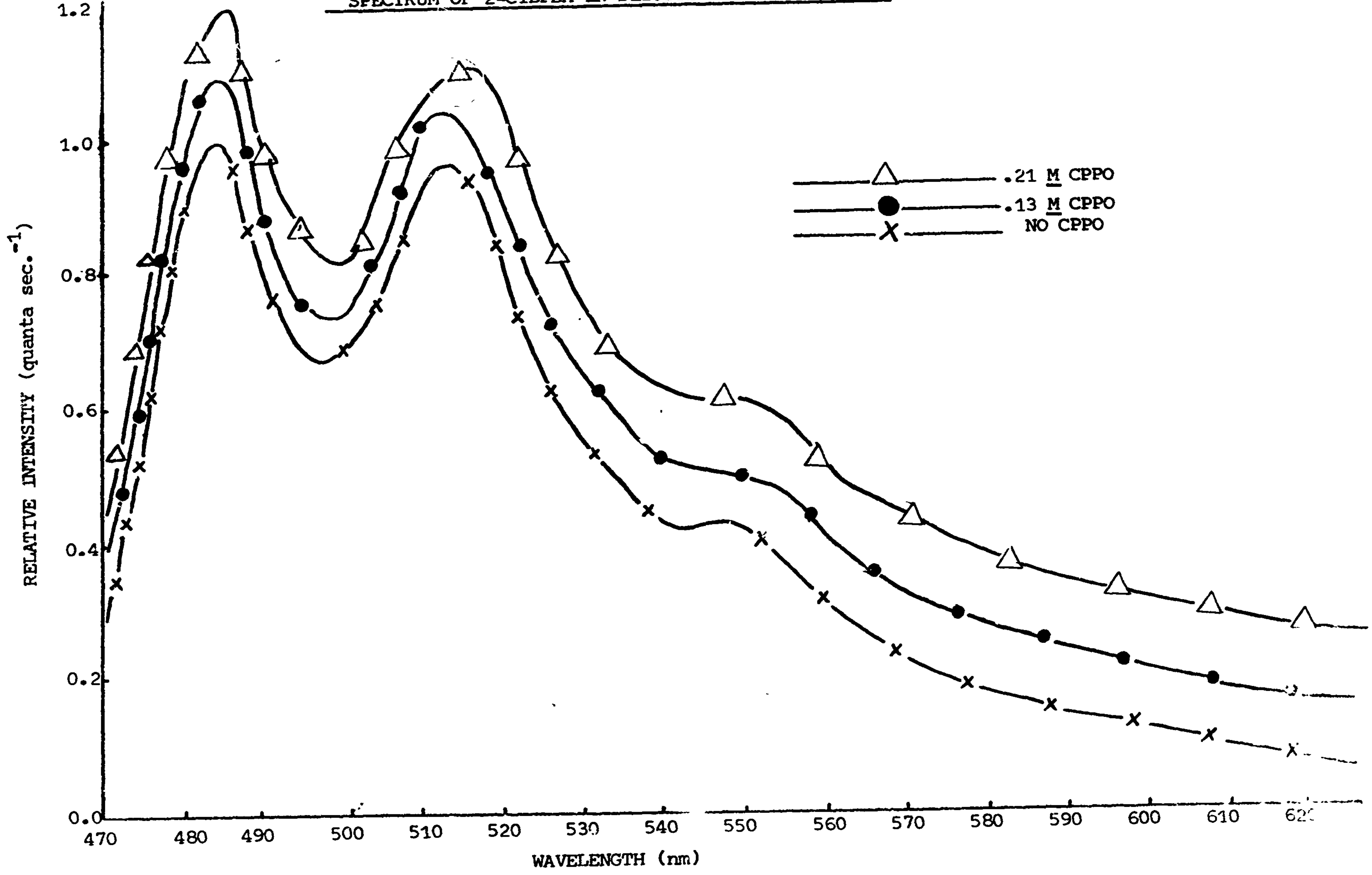


Footnotes to Figure 5b

a. Fluorescence spectra were measured on solutions containing .008 M 1-chloro-9,10-bis(phenylethynyl)anthracene (1-Cl BPEA) and the indicated concentrations of bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO) in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate, and 5% t-butanol. Excitation wavelength was 429 nm. The two upper spectra have been displaced by increments of 0.1 along the ordinate.

Figure 6

EFFECT OF CPPO CONCENTRATION ON THE FLUORESCENCE SPECTRUM OF 2-ClBPEA IN DIBUTYL PHTHALATE[a]



Footnotes to Figure 6

a. Fluorescence spectra were measured on solutions containing .003 M 2-chloro-9,10-bis(phenylethynyl)anthracene (2-Cl BPEA) and the indicated amounts of bis(2,4,5-trichloro-6-carbopentoxyphenyl) oxalate (CPPO) in dibutyl phthalate. Excitation wavelength was 429 nm. The two upper curves have been displaced by increments of 0.1 along the ordinate.

Table 25

Effect of Solvent on the Fluorescence Quantum Yield of 1-ClBPEA[a]

	Fluorescence Quantum Yield	
CPPO M	DBP[b]	DBP/DMP/TBA[c]
0	0.710	1.0
.10	0.646[d]	0.796
.21	0.584	0.716

a. Excitation wavelength 429.

b. Dibutyl phthalate, concentration of 1-ClBPEA, .003 M.

c. Solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol, concentration of 1-ClBPEA, .008 M.

d. Interpolated from Figure 2.

with maxima near 520 nm. No significant changes were evident in the spectral distributions over the course of the reactions. However, measurement of the spectral distribution of the emission from a chemiluminescent reaction containing 1-ClBPEA revealed that large spectral shifts take place during the first 90 minutes of reaction. Figure 7b illustrates the variation of the spectral distribution as a function of time in a typical reaction of .21 M CPPO, 0.375 M H_2O_2 and 0.008 M 1-ClBPEA. Within the first two minutes the spectrum shows a relatively sharp peak at 530 nm. As the reaction proceeds, the longer wavelength portion of the spectrum broadens and a new maximum is finally evident at 555 nm.

The change in spectral distribution as a function of time (Figure 7b) suggested that a new emitting species was being formed in the reaction. A comparison of the chemiluminescent and the fluorescence spectra or 1-ClBPEA is illustrated in Figure 8. The chemiluminescence spectrum reveals a large bathochromic shift (30 nm) with reference to the fluorescence emission. One might expect the shorter wavelength peak (500 nm) in fluorescence to be reduced in intensity from reabsorption in chemiluminescence, but the longer wavelength slope of the fluorescence spectrum should be nearly superimposable on the chemiluminescence spectrum. However, the difference between these spectra is probably too large to be accounted for on the basis of reabsorption alone. A similar but less pronounced effect was observed with 1,8-DCBPEA (Figure 9). This observation suggests that a new emitting species is being formed in the chemiluminescent reaction of 1-ClBPEA. A different emitting species may also be formed in the reaction of 1,8-DCBPEA, but the spectral distribution of the 1,8-DCBPEA reaction is constant with time so that new species, if present, must be formed very rapidly at the beginning of the reaction.

A convenient unit for expression of the rate of spectral broadening is the unit spectral area, the ratio of the total radiant energy output to the energy output at a specified wavelength (Figure 9).

The unit spectral area is used in our experiments to determine the total amount of radiant energy produced at any point in time during a chemiluminescent reaction from the energy output at a single wavelength. If the unit spectral area does not change during the decay experiment, then the total radiant energy and therefore the quantum yield and light capacity can be calculated from the intensity decay curve measured at a single wavelength.[11] The wavelength used for the chemiluminescent intensity decay experiments was 555 nm, since the relative intensity at this wavelength increases at the same rate as the spectral broadening so the unit spectral area remains constant with time. However, to use the unit spectral area as a measure of spectral broadening, we selected a wavelength (525 nm) near the initial maximum of the chemiluminescent spectral distribution. The change of the unit spectral area at this wavelength reflects the overall spectral changes.

The change of spectral distribution with time is an unusual phenomenom in peroxyoxalate chemiluminescence. The unexpectedly high efficiency of the 1-Cl BPEA system (described in Section IV-I) prompted us to study the effect of reaction variables on this spectral change since the efficiency may be a direct result of the observed spectral changes.

Figure 11 illustrates the effect of 1-ClBPEA concentration on the change of unit spectral area. Increasing the fluorescer concentration increases both the rate and extent of spectral broadening. Figure 12 indicates the CPPO concentration also has a substantial effect on the unit spectral area change. Note that the unit spectra area goes through a maximum at the highest CPPO concentration. This may indicate the new emitting species can be destroyed under these conditions. At 0.10 M CPPO only minor changes in spectral distribution are evident. However, as the CPPO concentration is increased to 0.21 M the spectral changes become much more pronounced. A comparison of the spectrum of the 0.21 M CPPO reaction recorded at the two minute point and the spectrum of the 0.10 M reaction measured after the unit spectral area has leveled off (60 minutes) is illustrated in Figure 13.

The two spectra are essentially identical. This suggests that the new emitting species is not present in any significant amount at any point in the 0.10 M CPPO reaction nor at the two minute point of the 0.21 M reaction. Increasing the concentration of sodium salicylate (to .001 M) or H_2O_2 (to 0.50 M) retards the extent of spectral change as indicated in Figure 14. An antioxidant, 2,6-dibutyl-4-methylphenol (DBPC), has no effect on the spectral change while the addition of a polyethylene oxide completely inhibits formation of the broadened spectrum.

In principle, the product of the CPPO - H_2O_2 reaction, pentyl-2,4,5-trichlorosalicylate (PTCS), might complex with 1-ClBPEA to form the new emitting species. However, the experiment illustrated in Figure 15 indicates this is not the case. No change in the rate of spectral broadening is evident when PTCS is present from the beginning of the reaction. Figure 15 also illustrates that the formation of the broadened spectrum is retarded by omitting the fluorescer from the reaction and adding it at the 30 minute point. This experiment confirms that formation of the new emitting species requires the presence of the fluorescer during the rapid phase of CPPO reaction, in agreement with the effects of CPPO and 1-ClBPEA concentration changes.

The change in spectral distribution derives from the formation of a species which emits at a longer wavelength than 1-ClBPEA (λ max. 530 versus 555). If a ground state species were responsible for the bathochromic shift of the chemiluminescent emission, one might expect a corresponding change in the absorption spectrum. In contrast, formation of an exiplex would not be evident from the absorption spectrum. A series of absorption spectra were measured on the undiluted chemiluminescent reaction in a thin (1 mm) cell. Figure 16 illustrates the change in absorbance at 510 nm versus time. The absorbance increases for the first 40 minutes of reaction and levels off to a constant value. This change parallels the change of unit spectral area measured from a similar reaction. However, when aliquots are removed from the reaction and diluted two hundred fold, no increase in absorbance nor any new bands are evident. Under the latter conditions, the concentration of fluorescer is found to decrease smoothly with time as found with other BPEA derivatives.

Although further experimental work is required to definitely establish the pathway by which the new emitting species is being formed in the reaction of 1-Cl BPEA , the scheme outlined in Chart IV represents one proposal which is consistent with the experimental evidence.

CHART IV

Tentative Mechanism for Spectral Change in the Chemiluminescent Reaction of 1-ClBPEA

$$\text{CPPO} + H_2O_2 \xrightarrow{\text{Fluorescer}} \text{X} \quad \text{(a by-product)} \qquad (1)$$

$$\text{Fluorescer} + \text{X} \rightleftharpoons (\text{Fluorescer} \cdot \text{X}) \qquad (2)$$

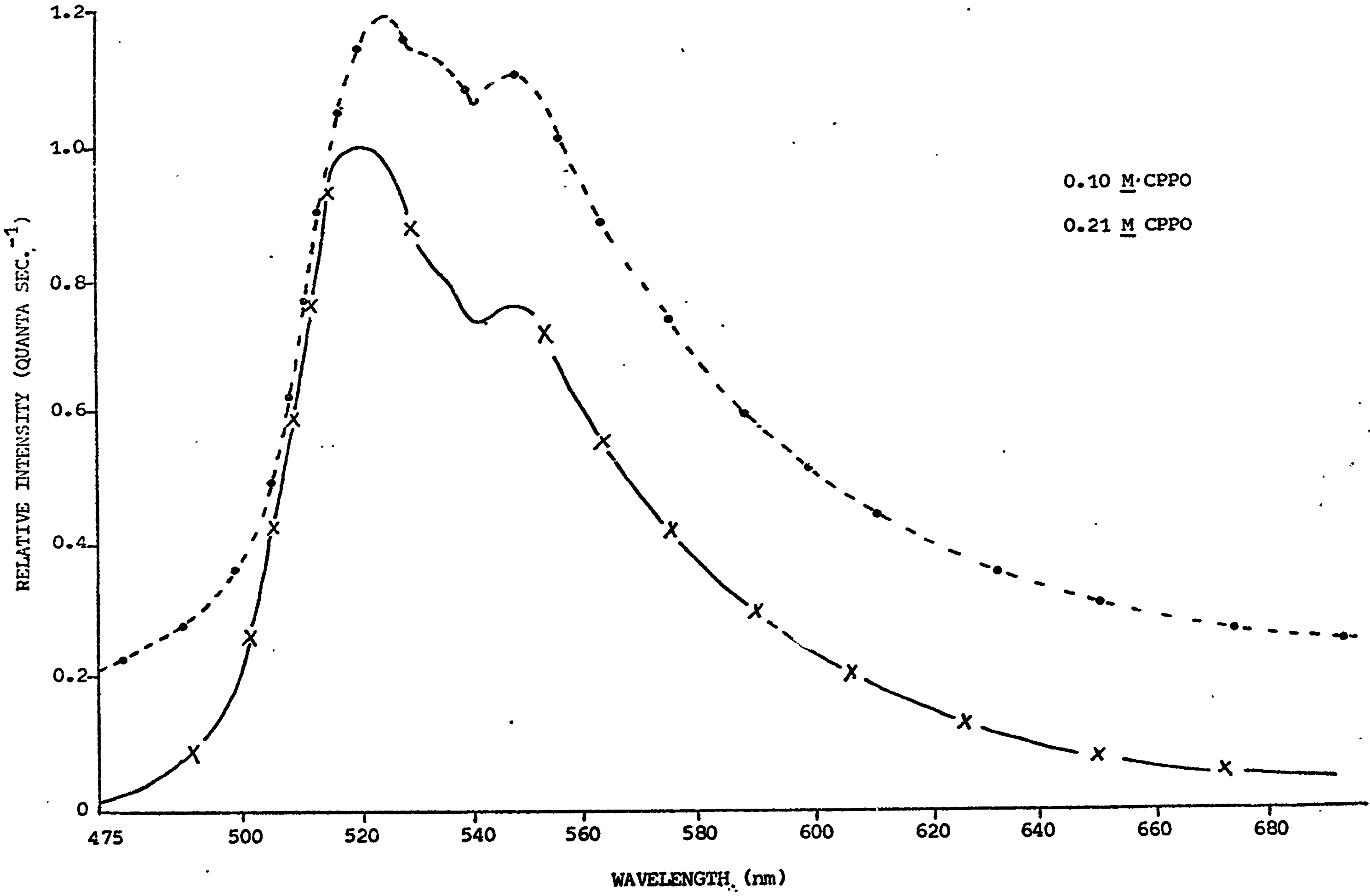
$$(\text{Fluorescer} \cdot \text{X}) + C_2O_4 \longrightarrow (\text{Fluorescer} \cdot \text{X})^* + 2CO_2 \qquad (3)$$

$$(\text{Fluorescer} \cdot \text{X})^* \longrightarrow (\text{Fluorescer} \cdot \text{X}) + h\nu \qquad (4)$$

A by-product, X, is produced by a side reaction which becomes important at CPPO concentrations on the order of .21 M. The concentration of X is thus dependent on CPPO concentration. However, increasing the rate of CPPO reaction by increasing the catalyst or H_2O_2 apparently decreases the concentration of X. This could be due to other side reactions consuming X which are promoted by these reagents. Since there is no evidence of the presence of X in a reaction carried out in the absence of 1-ClBPEA, it would appear either that 1-Cl BPEA stabilizes X from undergoing a destructive side reaction or that X is produced from a reaction involving both an intermediate derived from CPPO and 1-ClBPEA. In the second step, a charge-transfer complex is formed between the fluorescer and X (eq. 2). Increasing the fluorescer concentration thus favors the formation of this complex. This complex formation must be reversible since the absorption spectrum of the complex is no longer evident on dilution. The complex then undergoes

FIGURE 7a

EFFECT OF CPPO CONCENTRATION THE CHEMILUMINESCENT SPECTRAL DISTRIBUTION FROM 2-ClBPEA[a]



Footnotes to Figure 7a

a. Chemiluminescent reactions contained the indicated concentrations of bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), 0.375 M H_2O_2, and 0.007 M 2-chloro-9,10-bis(phenylethynyl)anthracene (2-ClBPEA) in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol. The 0.21 M CPPO reaction contained 5×10^{-4} M sodium salicylate and the 0.10 M reaction contained 1.56×10^{-4} M sodium salicylate. No significant changes in the spectral distributions were detected over the course of these reactions.

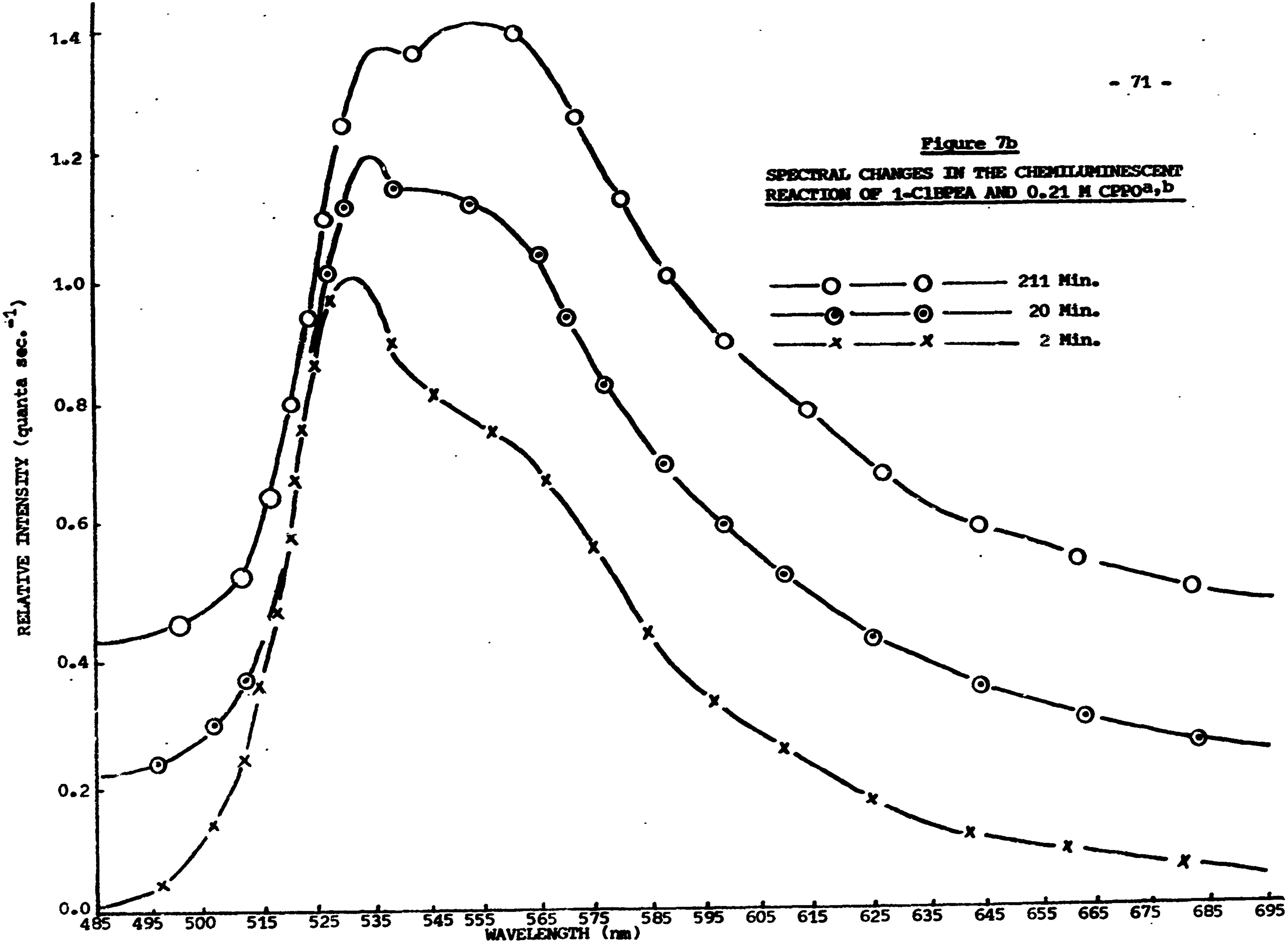


Figure 7b

SPECTRAL CHANGES IN THE CHEMILUMINESCENT REACTION OF 1-ClBPEA AND 0.21 M CPPO^{a,b}

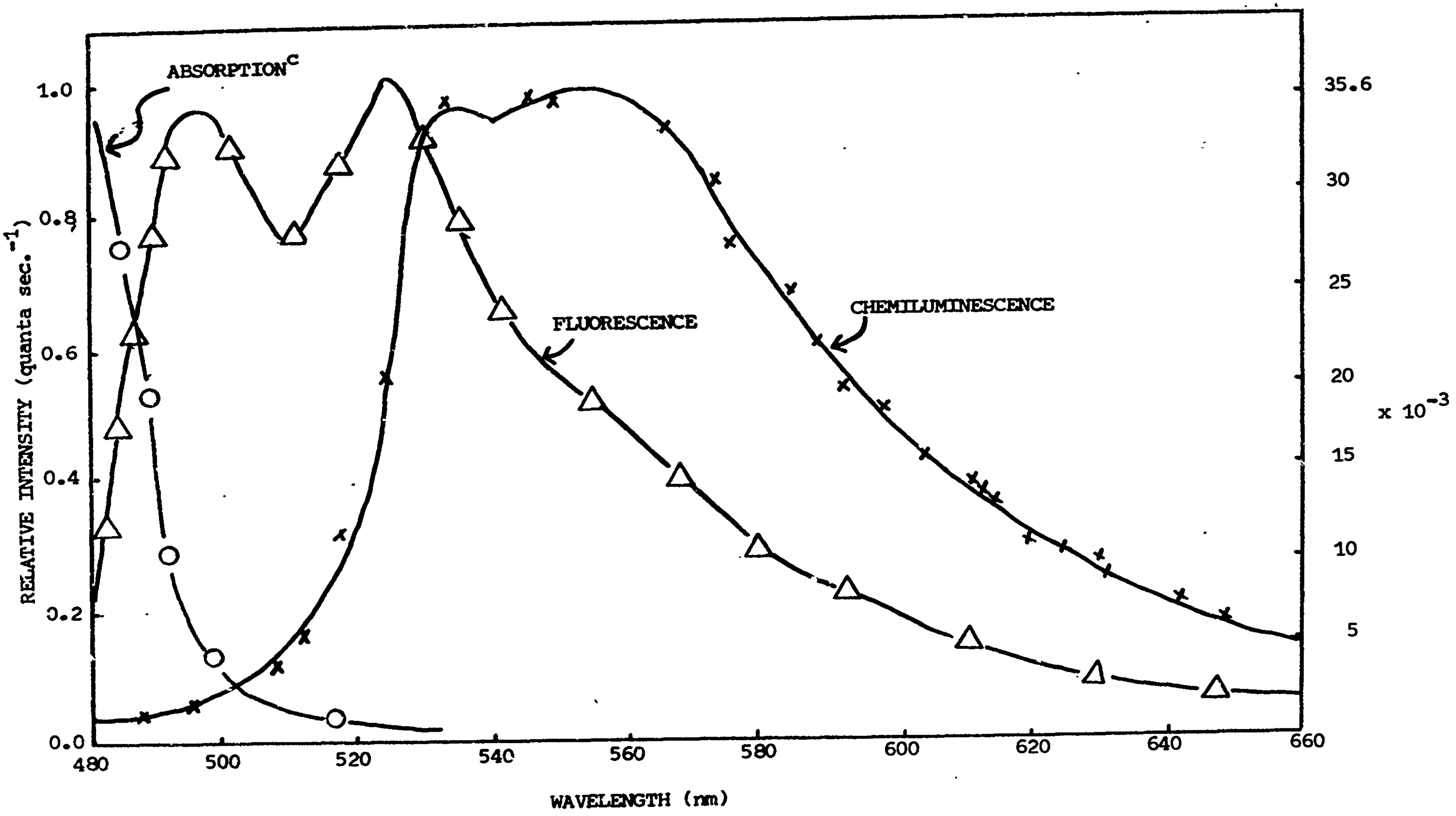
Footnotes to Figure 7b

a. Chemiluminescent reaction contained .21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), .375 M H_2O_2, 5×10^{-4} M sodium salicylate and .008 M 1-chloro-9,10-bis(phenylethynyl) anthracene (1-Cl BPEA) in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate and 5% t-butanol. Spectra are corrected for intensity decay.

b. The two upper spectra have been displaced by increments of 0.2 along the ordinate.

Figure 8

COMPARISON OF FLUORESCENCE[a] AND CHEMILUMINESCENCE[b] SPECTRA OF 1-ClBPEA



Footnotes to Figure 8

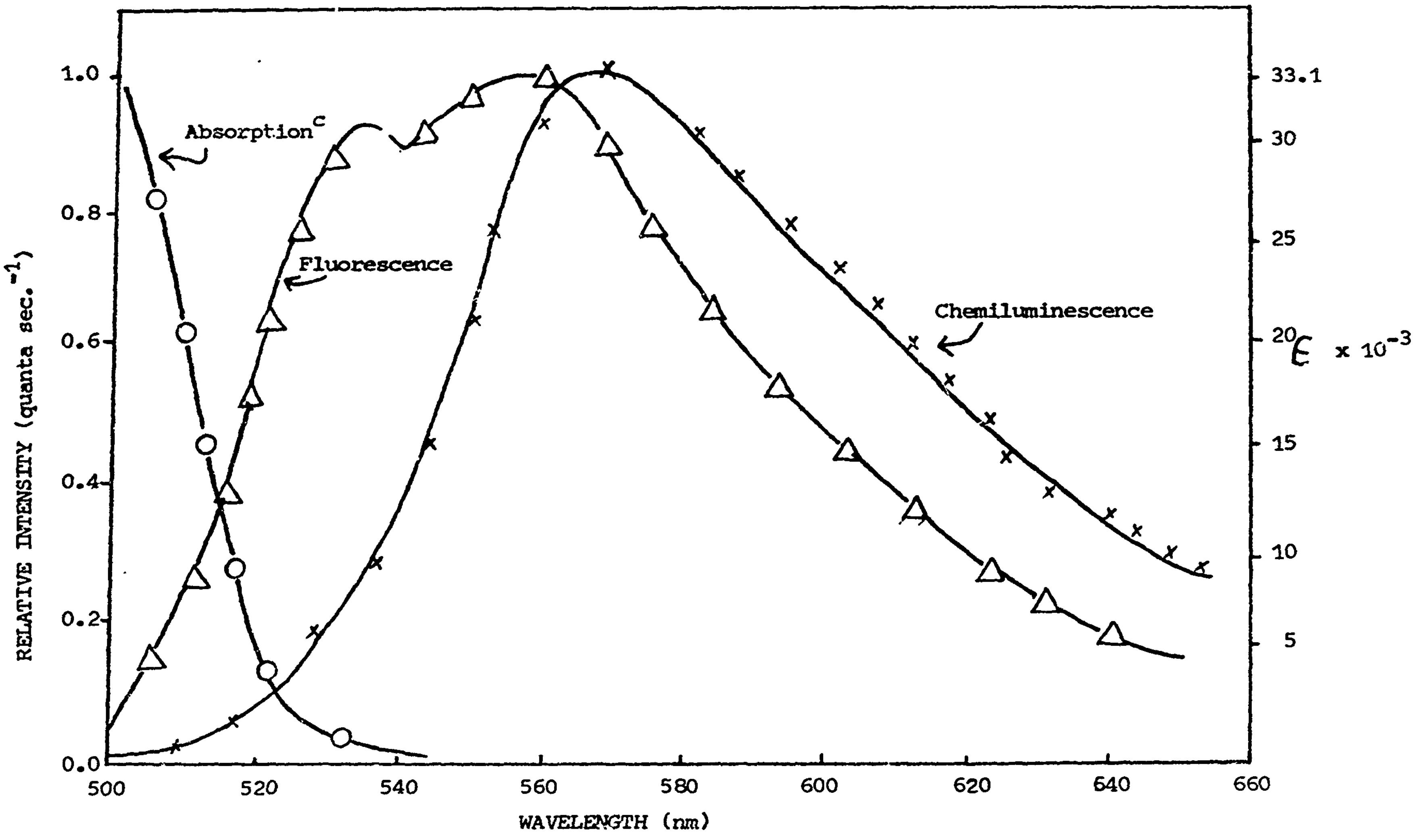
a. Fluorescence spectrum of a solution containing .008 M 1-chloro-9,10-bis(phenylethynyl)anthracene (1-Cl BPEA) and .21 M bis (3,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO) in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate and 5% t-butanol.

b. Chemiluminescence spectral distribution of a reaction containing .008 M 1-Cl BPEA, 0.21 M CPPO, 0.375 M H_2O_2 and 5 x 10^{-4} sodium salicylate in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate and 5% t-butanol. Spectrum was recorded 211 minutes after mixing the reagents and is corrected for intensity decay.

c. Absorption spectrum was measured on a sample containing 4 x 10^{-5} M 1-Cl BPEA in dibutyl phthalate.

Figure 9

COMPARISON OF CHEMILUMINESCENCE[a] AND FLUORESCENCE[b] SPECTRA OF 1,8-DCBPEA



Footnotes to Figure 9

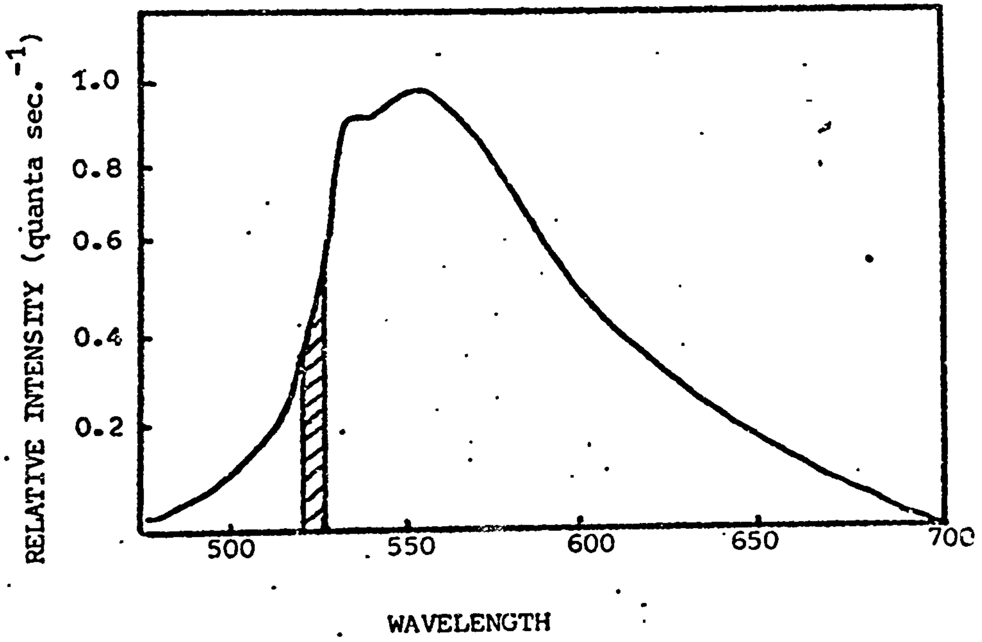
a. Chemiluminescence reaction contained .21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), 5.67×10^{-3} M 1,8-dichloro-9,10-bis(phenylethynyl)anthracene (1,8-DCBPEA), .375 M H_2O_2, 5×10^{-4} M sodium salicylate in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate and 5% t-butanol. Spectrum is corrected for intensity decay.

b. Fluorescence spectrum was measured on a solution containing .21 M CPPO and 5.67×10^{-3} M 1,8-DCBPEA in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate and 5% t-butanol. Excitation wavelength was 429 nm.

c. Absorption spectrum was measured on solution of 3.78×10^{-5} M 1,8-DCBPEA in dibutyl phthalate.

Figure 10

UNIT SPECTRAL AREA



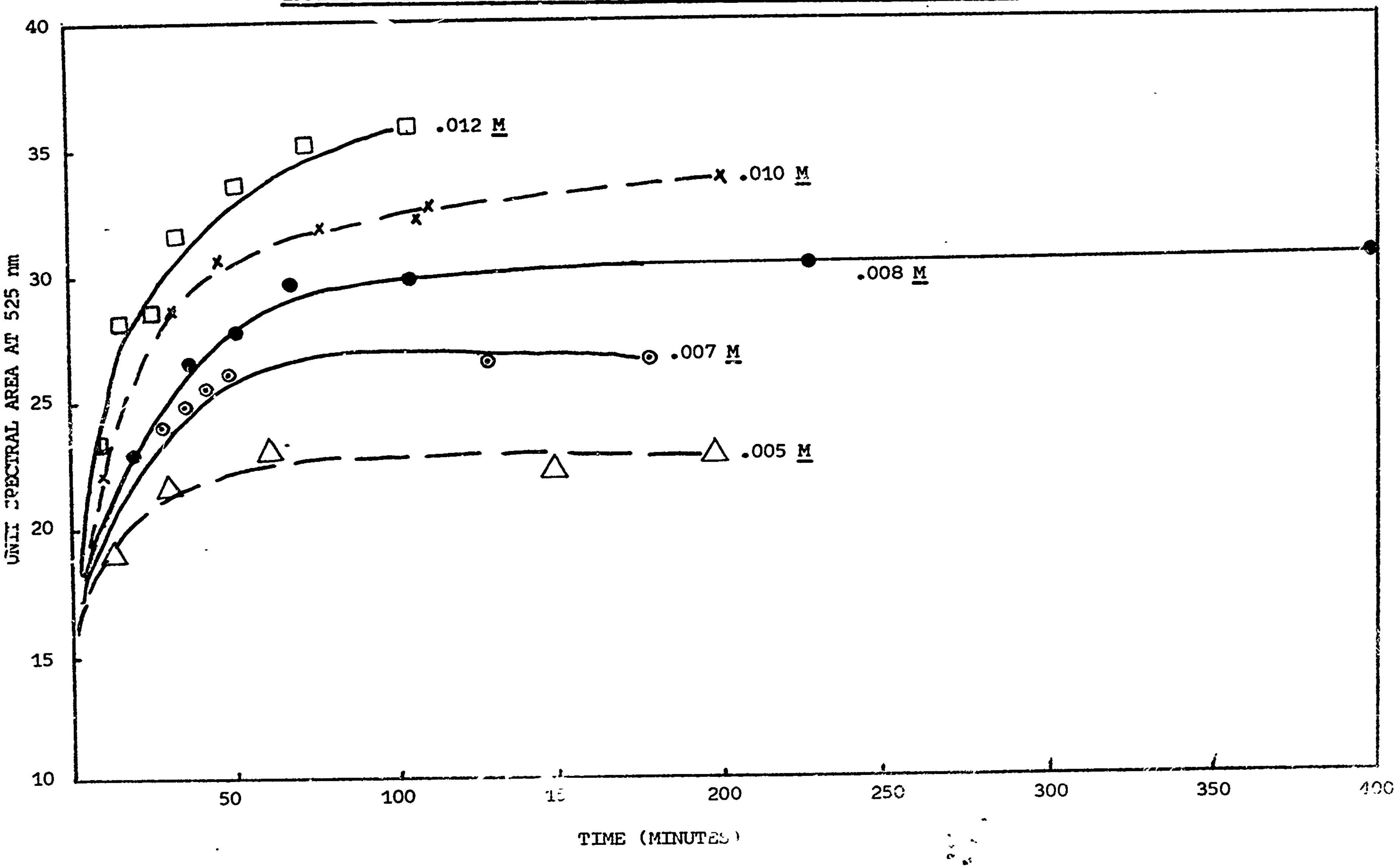
$$\text{Unit Spectral Area} = \frac{\text{Total Area Under Intensity Curve}}{\text{Shaded Area (at 525 nm)}}$$

$$\text{U. S. A.}^{a}_{525} = \frac{.9529 \times 10^{14} \text{ quanta sec.}^{-1}}{.3132 \times 10^{13} \text{ quanta sec.}^{-1}} = 30.43$$

a. Energy values from computer integration.

Figure 11

EFFECT OF 1-ClBPEA CONCENTRATION[a] ON UNIT SPECTRAL AREA[b] CHANGE



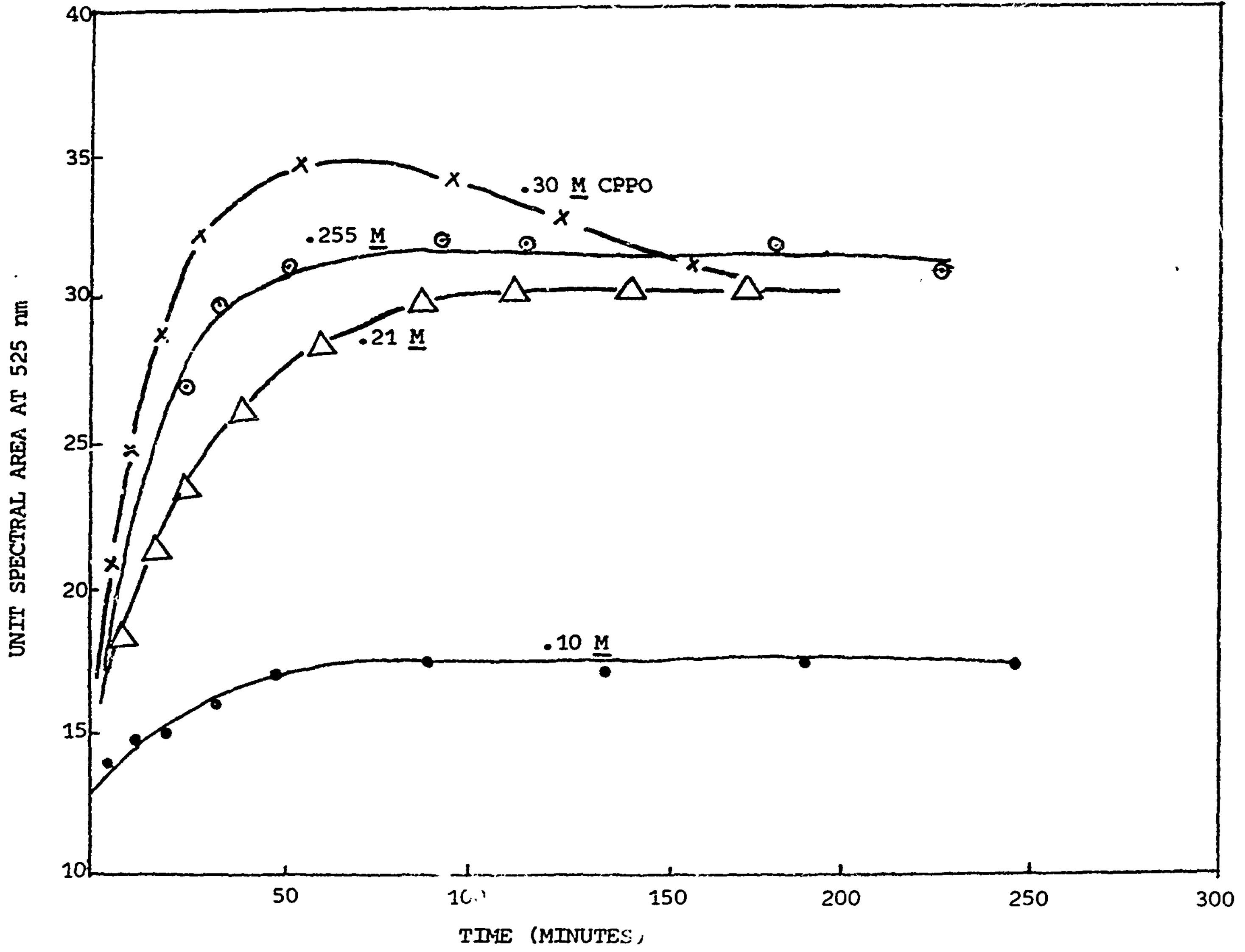
Footnotes to Figure 11

a. Chemiluminescent reactions contained 0.21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), 0.375 M H_2O_2, 5×10^{-4} M sodium salicylate and the indicated concentrations of 1-chloro-9,10-bis(phenylethynyl)anthracene (1-Cl BPEA) in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol.

b. Ratio of the total radiant energy emitted (in quanta $sec.^{-1}$) from 485 nm to 695 nm to the energy emitted at 525 nm.

Figure 12

EFFECT OF CPPO CONCENTRATION^a ON UNIT SPECTRAL AREA^b CHANGE



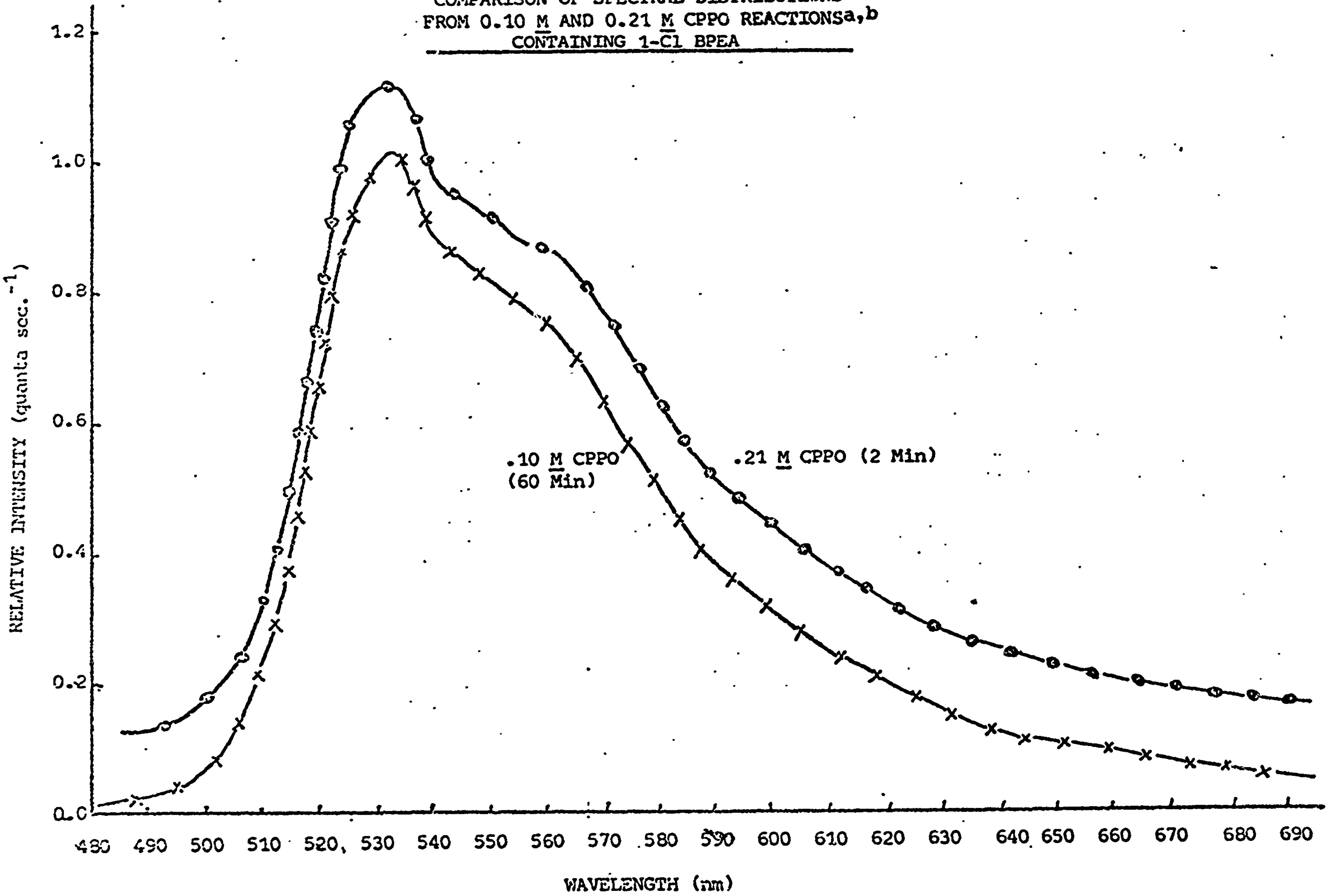
Footnotes to Figure 12

a. Chemiluminescent reactions contained .008 M 1-chloro-9,10-bis(phenylethynyl)anthracene (1-Cl BPEA), 0.375 M H_2O_2 and the indicated concentrations of bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO). The 0.10 M CPPO reaction contained 1.56×10^{-4} M sodium salicylate (NaSal) and the higher CPPO concentrations contained 5×10^{-4} M NaSal. Solvent mixture was 75% dibutyl phthalate, 20% dimethyl phthalate and 5% t-butanol.

b. Ratio of the total radiant energy emitted (in quanta $sec.^{-1}$) from 485 nm to 695 nm to the energy emitted at 525 nm.

Figure 13

COMPARISON OF SPECTRAL DISTRIBUTIONS
FROM 0.10 M AND 0.21 M CPPO REACTIONSa,b
CONTAINING 1-Cl BPEA



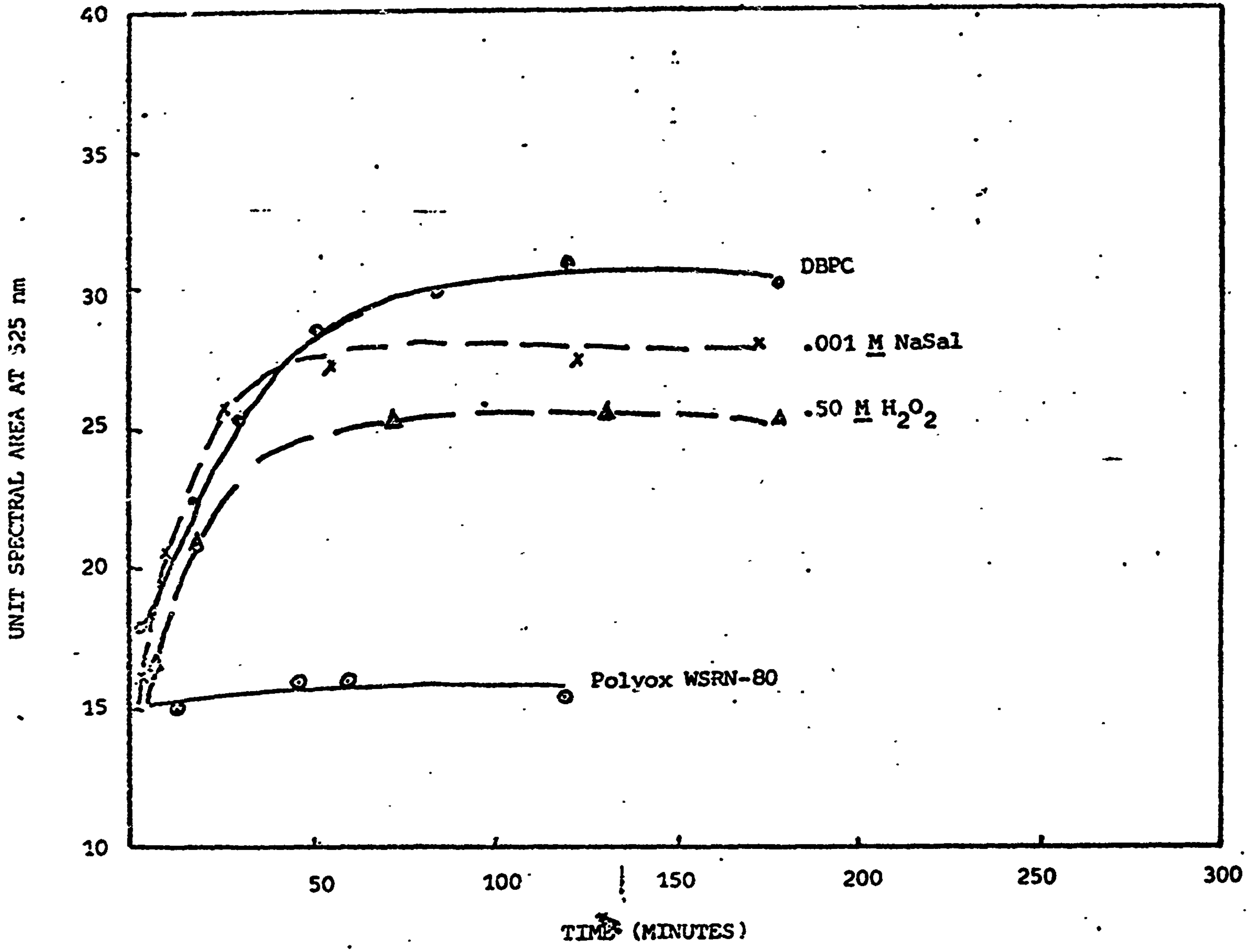
Footnotes to Figure 13

a. Chemiluminescent reactions contained .375 M H_2O_2, 0.008 M 1-chloro-9,10-bis(phenylethynyl)anthracene (1-Cl BPEA) and the indicated concentrations of bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO) in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate, and 5% t-butanol. The 0.10 M CPPO reaction contained 1.56×10^{-4} M sodium salicylate (NaSal) and the 0.21 M CPPO reaction contained 5×10^{-4} M NaSal. Spectra have been corrected for intensity decay.

b. The 0.21 M CPPO spectrum has been displaced by 0.1 along the ordinate.

Figure 14

EFFECT OF ADDITIVES, SODIUM SALICYLATE AND H_2O_2[a] ON UNIT SPECTRAL AREA[b] CHANGE



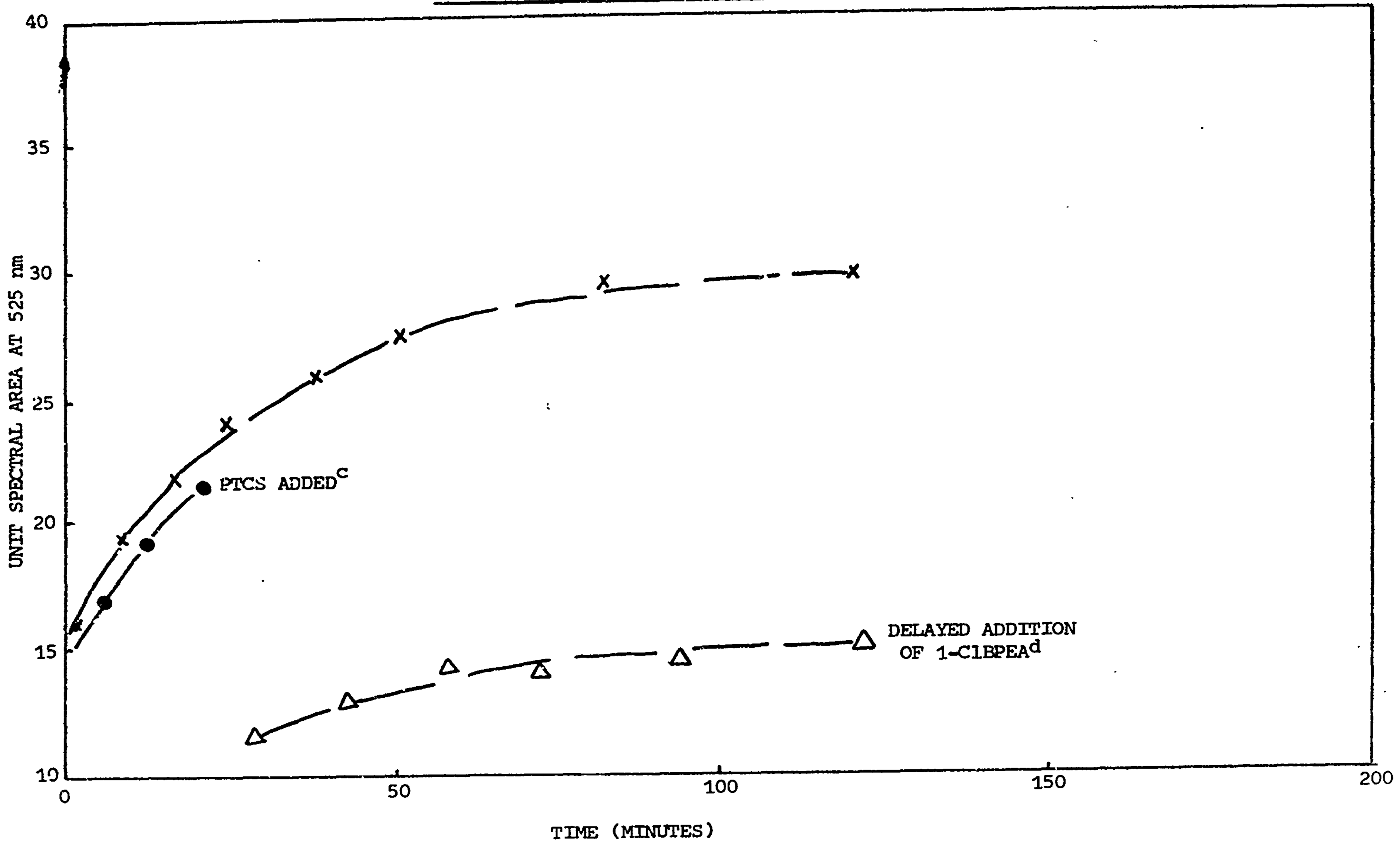
Footnotes to Figure 14

a. Unless otherwise indicated chemiluminescent reactions contained 0.21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), 0.008 M 1-chloro-9,10-bis(phenylethynyl)anthracene (1-Cl BPEA), 0.375 M H_2O_2 and 5 x 10^{-4} sodium salicylate (NaSal) in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate and 5% t-butanol. Additives used: 2,6-di-t-butyl-p-cresol (DBPC) and polyethylene oxide (Polyox WSRN-80).

b. Ratio of the total radiant energy output from 485 nm to 695 nm to the energy emitted at 525 nm.

Figure 15

EFFECT OF PTCS AND DELAYED FLUORESCER ADDITION[a] ON UNIT SPECTRAL AREA[b] CHANGE



Footnotes to Figure 15

a. Unless indicated otherwise chemiluminescent reactions contained 0.21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), 0.375 M H_2O_2, 5 x 10^{-4} M sodium salicylate and .008 M 1-chloro-9,10-bis-(phenylethynyl)anthracene (1-Cl BPEA) in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate and 5% t-butanol.

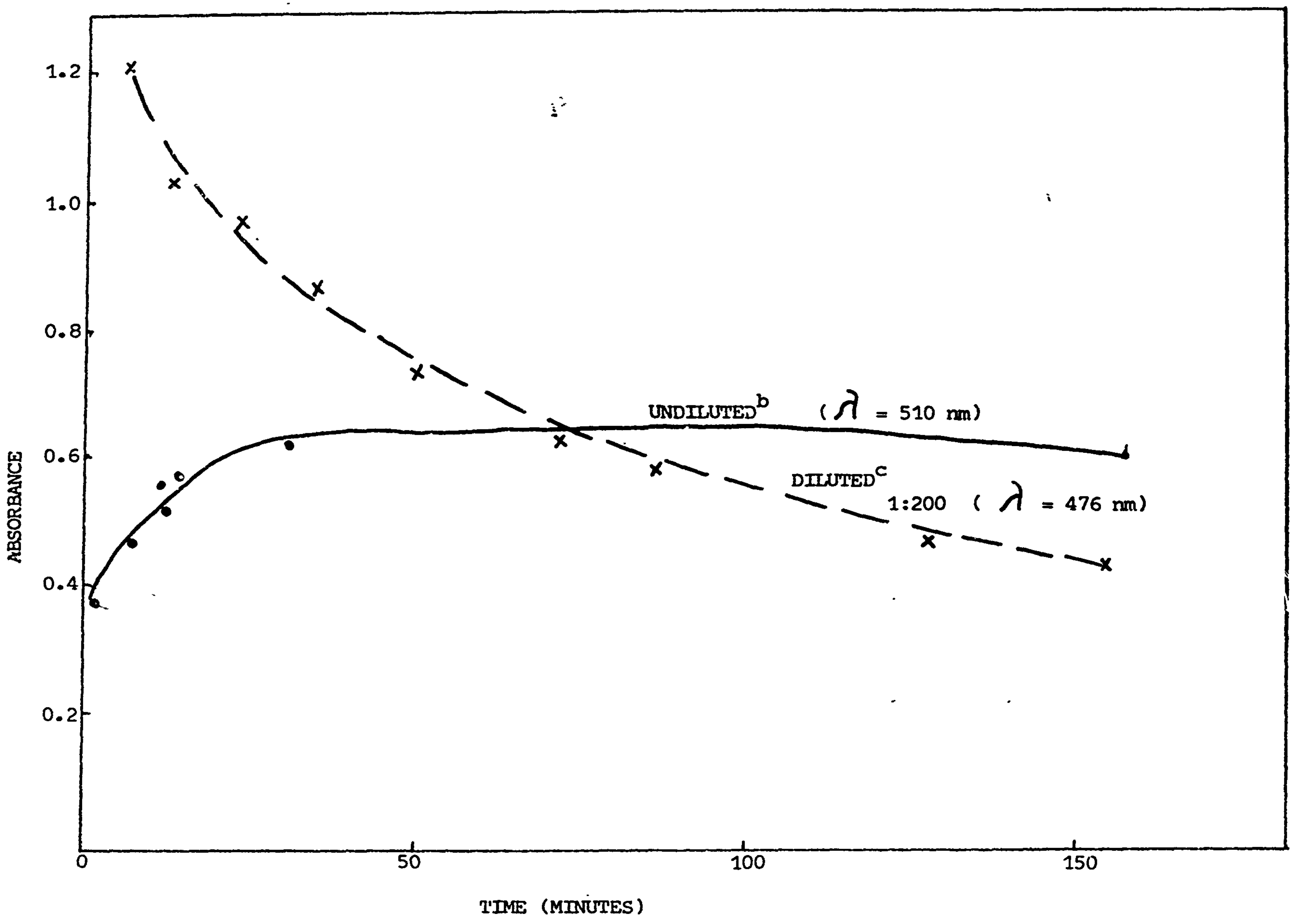
b. Ratio of the total radiant energy output from 485 nm to 695 nm to the energy emitted at 525 nm.

c. This reaction initially contained .105 M pentyl-3,5,6-trichlorosalicylate (PTCS), .158 M CPPO and .006 M 1-Cl BPEA. This corresponds to 25% of the CPPO consumed in a typical 0.21 M CPPO reaction.

d. The 1-Cl BPEA was omitted from the reaction and added at the 30 minute point. Final concentrations are as in footnote a (above).

Figure 16

ABSORBANCE VS. TIME IN CHEMILUMINESCENT REACTION[a] OF 1-ClBPEA



Footnotes to Figure 16

a. Chemiluminescent reaction contained .21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), .375 M H_2O_2, .008 M 1-chloro-9,10-bis(phenylethynyl)anthracene (1-Cl BPEA) and 5 x 10^{-4} sodium salicylate in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate and 5% t-butanol. Spectral measurements were carried out on a Cary 14 spectrophotometer using reversed optics to minimize contribution from the chemiluminescence emission.

b. This sample contained the reaction mixture described in "a" (above) in a 1 mm cell. Absorbance was measured at 510 nm.

c. An aliquot of the reaction mixture was diluted 200 fold with dibutyl phthalate and the absorbance measured at 476 nm (the absorption maximum of 1-Cl BPEA).

excitation by the key intermediate in the usual manner providing a lower energy pathway (eq. 4) for release of the energy of the key intermediate, and emission is observed at a longer wavelength than from the fluorescer itself

The high efficiency observed from the 1-ClBPEA reaction could be related to an increase in excitation yield resulting from the lower excitation energy of the complex.[12,13] The mechanism proposed here is necessarily speculative due to the limited experimental results available. However, the observation that large spectral changes can be produced by compounds present in the chemiluminescent reaction deserves much closer investigation since the potential of producing high light output is promising. Moreover, if the "X" species can be identified it may be possible to increase the efficiency of current chemical light systems and/or produce a bathochromic shift of the spectral distribution by adding "X" or a similar compound to the reaction.

I. Chemiluminescent Performance of 1-ClBPEA and 2-ClBPEA

The chemiluminescent performance obtained with 2-ClBPEA at two concentrations of CPPO, 0.10 M and 0.21 M, is summarized in Table 26. Light capacities at the lower CPPO concentration were in the range of 420-460 and in the range of 680-730 at the high CPPO level. Concentration quenching is evident as the quantum yield decreases by about 25% on increasing the concentration of CPPO two fold.

Initial results on the chemiluminescent performance of 1-ClBPEA indicated that higher efficiencies were obtained by use of this fluorescer than with 2-ClBPEA. These results together with better solubility for 1-ClBPEA prompted us to study its chemiluminescence performance in more detail. The effect of fluorescer concentration on the efficiency of chemiluminescent reactions containing 0.10 M CPPO is summarized in Table 27. High light capacities (520-575 lumen hours liter^{-1}) were found for all the 1-ClBPEA concentrations studied, with the corresponding quantum yields (16-18%) being particularly encouraging.

The intensity decay curve shape of the 1-ClBPEA system is compared to the BPEA system in Figure 17. The 0.10 M CPPO-1-ClBPEA system provides a more efficient distribution of the available light with respect to time than either BPEA at 0.10 M CPPO or 1-ClBPEA at 0.21 M CPPO.

The effect of 1-ClBPEA concentration at 0.21 M CPPO is summarized in Table 28. Light capacity values above 800 lumen hours liter^{-1} were found for all the reactions within the range of 1-ClBPEA concentrations investigated. The optimum concentration of fluorescer (.007 M in the chemiluminescent reaction) provided the highest light capacity yet reported, 900 lumen hours liter^{-1} (average of two experiments). The effect of sodium salicylate and H_2O_2 concentrations and effects of certain additives on the chemiluminescent performance of 1-ClBPEA at the 0.21 M CPPO concentration is summarized in Table 29. A two fold increase in the concentration of catalyst produces a very bright system and reduces the T.75 lifetime by about half. This formulation could be effective for illumination applications and in marker applications where long lifetime is not critical. The high intensity formulation may also be useful in low temperature environments. A 25% increase in H_2O_2 concentration slows the reaction rate slightly and provides a better distribution of the light intensity without significant change in light capacity. The antioxidant, DBPC, causes an 8% reduction in light capacity, principally due to lower intensity values beyond two hours. The addition of Polyox reduces the light capacity by 17%. This decrease is associated with the absence of spectral change as discussed earlier.

The sodium and tetrabutylammonium salts of salicylic acid have been shown[2,3] to be effective catalysts in oxalate chemiluminescent reactions at low catalyst concentration (ca. 10^{-3} - 10^{-4} M). We sought to study the effect of w[illegible] bases on the 0.21 M CPPO system since a higher base concentration [illegible] be [illegible]cial in neutralizing trace amounts of acidic contaminants which can [illegible]ion periods. In principle, an alkali metal or tetra alkylammonium salt of [illegible]ger acid than salicylic should be a weaker base. The relative acidities of salicylic acid (pKa = 2.97) and 3,5,6-trichlorosalicylic acid (pKa = 1.85) indicated that a salt of the trichloro acid might be effective. Concurrent studies[9] in a company sponsored program indicated that the tetramethylammonium salt of 3,5,6-trichlorosalicylic acid (TMATS) might be the most effective from both stability and performance criteria. The data summarized in Table 30 illustrates the effect of the concentration of TMATS on the performance of formulations containing 0.007 $\underline{M}$ 1-ClBPEA and 0.21 $\underline{M}$ CPPO. At the lowest concentration (10^{-4} $\underline{M}$) a system was produced which provided a brightness level above two foot lamberts cm^{-1} for more than 15 hours. This formulation could be useful to the military in overnight marking applications where high brightness is not required. Increasing the concentration of catalyst shortens the lifetime but does not produce the high initial intensities which are observed with sodium salicylate. Omission of a catalyst from this system causes a severe loss in light output (light capacity of 80 to 95 lumen hours $liter^{-1}$). A progressive decrease in light capacity is also observed with increasing concentrations of TMATS.

The effect of CPPO concentration on the efficiency of chemiluminescent reactions containing 1-ClBPEA is summarized in Table 31. The quantum yield decreases with increasing concentration of CPPO, but concentration quenching does not become severe until above 0.21 $\underline{M}$. Oxalate components supersaturated with CPPO were used in two of these experiments (.255 $\underline{M}$ and .30 $\underline{M}$ CPPO in the reaction) to ascertain whether modifying the basic CPPO structure to increase solubility would be a practical approach to higher light output. The data indicate that a new oxalate ester is probably required for increases in light capacity above the 900 lumen hours $liter^{-1}$ level. However, development of an oxalate ester which maintains the current 14% quantum yield at 0.4 $\underline{M}$ concentration would give a light capacity of nearly 1700 lumen hours $liter^{-1}$.

Table 26

CHEMILUMINESCENT PERFORMANCE OF 2-Cl BPEA[a]

2-Cl BPEA	CPPO	NaSal		Q. Y.		Intensity (Ft. Lmbt. cm^{-1}) vs. Time (Minutes)							
M	M	M x 10^4	Lt. Cap.	x 10^2	T·75	2	10	30	60	90	120	180	240
.005	.10	1.56	448	14.9	118	31.3	28.1	24.9	16.6	10.4	6.2	2.8	1.6
.005	.10	1.56	457	15.2	116	33.3	28.9	25.2	16.9	10.5	6.3	2.9	1.6
.007[b]	.10	1.56	431	14.2	106	30.3	26.3	24.7	17.4	10.9	6.4	2.6	1.3
.007[b]	.10	1.56	421	13.9	104	30.4	26.5	24.3	17.1	10.8	6.2	2.6	1.3
.005	.21	5.0	703	11.0	106	71.0	61.4	37.9	22.0	14.8	9.7	4.7	2.5
.005	.21	5.0	682	10.6	111	70.5	59.0	35.9	21.1	14.3	9.4	4.7	2.5
.007[b]	.21	5.0	686	10.7	108	63.0	54.6	35.8	23.0	16.3	10.9	4.3	2.1
.007[b]	.21	5.0	730	11.4	112	66.3	57.4	38.0	24.0	17.0	11.5	5.3	2.6

a. Chemiluminescent reactions contained 0.21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), 0.375 M H_2O_2 and the indicated concentrations of sodium salicylate (NaSal) and 2-chloro-9,10-bis(phenylethynyl)-anthracene (2-Cl BPEA) in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate and 5% t-butanol.

b. On standing the fluorescer precipitated from the oxalate components corresponding to these reactions. Solutions were warmed to dissolve the fluorescer and cooled to room temperature before mixing with the activator component.

Table 27

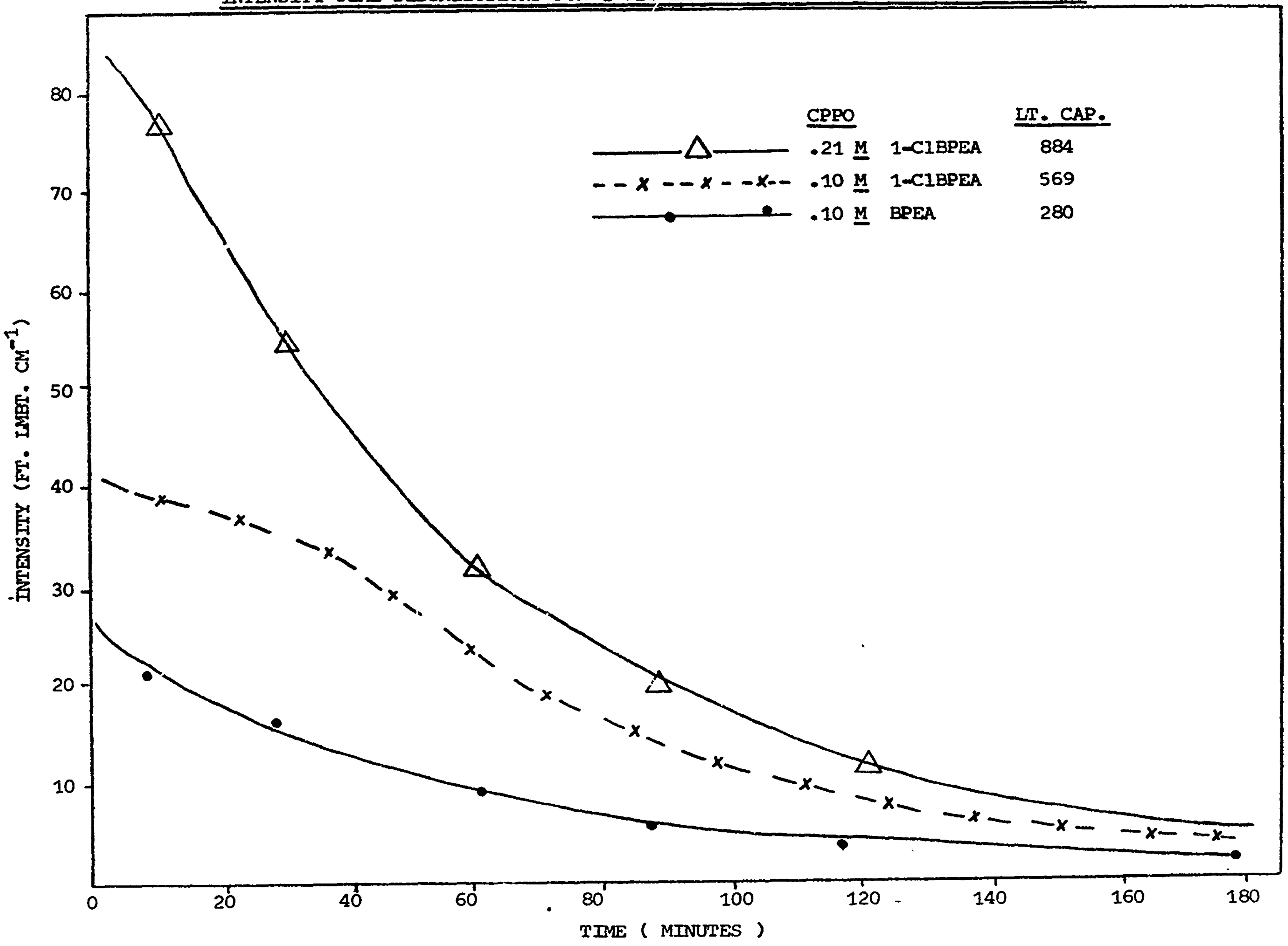
EFFECT OF 1-Cl BPEA CONCENTRATION ON CHEMILUMINESCENCE PERFORMANCE AT .10 M CPPO[a]

Conc. 1-Cl BPEA M	Lt. Cap.	Q. Y. x 10^2	T.75	Intensity (Ft. Lmbt. cm^{-1}) vs. Time (Minutes)					
				2	10	30	60	90	120
.005	569	17.9	98	41.3	38.6	35.0	23.6	13.9	8.1
.005	552	17.3	97	41.1	38.1	34.1	22.6	13.2	7.9
.006	577	17.9	98	40.1	37.6	34.9	24.4	14.6	8.6
.006	541	16.8	99	37.5	35.2	32.8	22.6	13.4	7.9
.007	574	18.0	99	39.4	36.3	34.7	25.3	15.1	8.9
.007	523	16.5	97	37.6	34.5	32.3	22.7	13.2	7.8
.008	535	16.8	101	34.2	32.6	31.7	23.5	14.4	8.5
.008	522	16.4	98	34.4	32.0	31.5	23.2	11.1	8.1

a. Chemiluminescent reactions contained 0.10 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), .375 M H_2O_2, 1.56 x 10^{-4} M sodium salicylate and the indicated concentrations of 1-chloro-9,10-bis(phenylethynyl)anthracene (1-Cl BPEA) in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate and 5% t-butanol.

Figure 17

INTENSITY-TIME DISTRIBUTIONS FOR 1-ClBPEA AND BPEA CHEMILUMINESCENT SYSTEMS[a]



Footnotes for Figure 17

a. Chemiluminescent reactions contained the indicated amounts of bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO). The 0.21 M CPPO reaction contained .007 M 1-chloro-9,10-bis(phenylethynyl)anthracene (1-ClBPEA), 5×10^{-4} M sodium salicylate (NaSal). The 0.10 M CPPO reactions contained .005 M 1-ClBPEA or 2.25×10^{-3} M 9,10-bis(phenylethynyl)anthracene (BPEA) and 1.56×10^{-4} M NaSal. All three reactions employed 0.375 M H_2O_2 and a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate and 5% t-butanol.

Table 28.

EFFECT OF FLUORESCER CONCENTRATION ON CHEMILUMINESCENT PERFORMANCE OF 1-Cl BPEA AT 0.21 M CPPO[a]

Conc 1-Cl BPEA M	Lt. Cap.	Q. Y. x 10^2	T.75	Intensity versus Time							
				2	10	30	60	90	120	180	240
.005	840	12.9	81	89.0	81.4	53.7	29.1	16.0	9.1	3.8	2.0
.005	819	12.6	72	88.5	79.2	51.8	28.3	16.1	8.9	3.7	2.2
.007	920	14.4	92	85.0	78.9	56.0	33.8	19.9	11.6	4.8	2.5
.007	884	13.9	91	84.0	75.9	53.9	32.2	19.0	11.2	4.6	2.4
.008	883	13.9	98	79.5	72.2	51.3	31.6	19.6	11.4	4.6	2.4
.008	866	13.7	107	81.0	69.4	46.8	29.8	19.8	12.9	5.7	2.8

a. Chemiluminescent reactions contained 0.21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate, 0.375 M H_2O_2, 5 x 10^{-4} M sodium salicylate and the indicated concentrations of 1-chloro, 9,10-bis(phenylethynyl)anthracene (1-Cl BPEA) in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate and 5% t-butanol.

Table 29

EFFECT OF CATALYST, H_2O_2 AND ADDITIVES ON CHEMILUMINESCENT PERFORMANCE OF 1-Cl BPEA[a]

NaSal M x 10^4	H_2O_2 M	Additive	Lt. Cap.	Q. Y. x 10^2	T.75	Intensity versus Time 2	10	30	60	90	120	180	24
5	.375	---------	883	13.9	98	79.5	72.2	51.3	31.6	19.6	11.4	4.6	2.
10	.375	---------	880	13.7	46	151.0	117.0	67.6	31.9	9.4	3.2	0.6	0.
5	.50	---------	872	13.5	124	63.4	58.8	44.4	30.3	20.5	14.2	7.5	4.
5	.50	---------	882	13.7	129	62.8	58.0	44.1	30.2	20.6	14.3	7.4	4.
5	.375	DBPC[b]	817	13.1	78	75.5	68.1	51.4	35.0	21.8	11.0	2.7	0.
5	.375	Polyox[b]	734	11.2	147	41.2	30.0	30.9	25.8	20.9	15.1	7.6	4.

a. Chemiluminescent reactions contained .21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), .008 M 1-chloro-9,10-bis(phenylethynyl)anthracene and the indicated concentrations of H_2O_2 and sodium salicylate (NaSal) in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate, and 5% t-butanol.

b. Concentrations of additives used: polyethylene oxides (Polyox WSRN-80), 0.15%; 2,6-di-t-butyl-p-cresol (DBPC), 3.75 x 10^{-4} M.

Table 30

PERFORMANCE OF 1-ClBPEA CHEMILUMINESCENT SYSTEMS CONTAINING TETRAMETHYLAMMONIUM 3,5,6-TRICHLOROSALICYLATE (TMATS)[a]

Conc. TMATS $M \times 10^4$	Lt. Cap.[b]	Q. Y.[c] $\times 10^2$	T·75[d]	Intensity (Ft. Lamberts cm^{-1}) versus Time 0 Min.	2 Min.	10 Min.	30 Min.	1 Hr.	2 Hr.	3 Hr.	4 Hr.	5 Hr.	8 Hr.	10 Hr.	12 Hr.	14 Hr.
1.0	888[e]	13.9	877	11.7	12.9	13.7	11.6	9.6	7.2	6.2	5.4	4.4	3.7	3.2	2.8	2.3
1.0	978[e]	15.3	889	14.2	16.0	14.9	12.4	10.1	7.6	6.6	5.8	4.8	4.1	3.6	3.2	2.7
1.56	907	14.2	444	29.5	24.5	18.0	14.6	12.2	10.7	8.5	8.0	7.7	5.6	3.3	1.9	1.0
1.56	933	14.6	443	28.3	19.0	16.7	15.3	13.2	11.2	9.1	8.4	7.9	5.6	3.4	1.9	1.1
3.0	919	14.4	245	54.1	37.4	28.9	24.3	20.8	16.7	13.3	10.3	4.8	2.0	---	---	---
3.0	911	14.3	244	54.8	37.0	28.5	24.0	20.6	16.6	13.2	10.3	4.8	2.0	---	---	---
5.0	863	13.5	151	79.0	51.9	40.6	36.7	27.7	19.2	11.9	6.1	1.0	0.1	---	---	---
5.0	862	13.5	150	78.6	51.9	40.3	33.8	28.0	19.2	11.9	6.1	0.9	0.1	---	---	---
7.5	782	12.2	119	65.7	59.5	45.5	37.1	28.5	17.1	7.8	---	---	---	---	---	---
7.5	837	13.1	127	65.6	59.2	46.5	38.2	29.7	17.7	8.6	---	---	---	---	---	---
10.0	752	11.8	84	86.5	79.0	61.6	44.7	30.3	13.0	2.9	---	---	---	---	---	---
10.0	736	11.5	84	83.7	76.5	60.1	44.1	30.6	12.9	2.9	---	---	---	---	---	---
5.0[f]	926	14.5	107	102.	74.3	69.2	51.2	34.6	13.1	5.6	2.9	1.2	0.7	---	---	---
5.0[f]	934	14.6	106	102.	75.3	70.1	51.8	34.9	13.0	5.5	2.9	1.2	0.7	---	---	---

a. Chemiluminescent reactions contained 0.21 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate, .007 M 1-chloro-9,10-bis(phenylethynyl)anthracene, 0.375 M H_2O_2 and the indicated concentration of catalyst in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol.

b. Light capacity in lumen hours liter^{-1}.

c. Quantum yield in einsteins mole^{-1}.

d. Time required for emission of 75% of the total amount of light.

e. The extrapolated portion of the total decay area in these experiments was 28%.

f. Sodium salicylate was used as the catalyst in these experiments.

Table 31

EFFECT OF CPPO CONCENTRATION ON CHEMILUMINESCENCE PERFORMANCE OF 1-Cl BPEA[a]

CPPO M	Lt. Cap.	Q. Y. x 10^2	T.75	Intensity versus Time (Min.) 2	10	30	60	90	120	180	240
.10[b]	535	16.8	101	34.2	32.6	31.7	23.5	14.4	8.5	3.6	----
.21	883	13.9	98	79.5	72.2	51.3	31.6	19.6	11.4	4.6	2.4
.25[c]	835	10.9	97	69.6	70.8	48.3	30.7	18.8	11.6	5.1	2.6
.30[c]	754	8.41	94	66.8	64.2	44.2	30.0	17.7	11.3	4.2	1.9

a. Chemiluminescent reactions contained the indicated concentrations of bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), .008 M 1-chloro-9,10-bis(phenylethynyl)anthracene (1-Cl-BPEA), 5 x 10^{-4} M sodium salicylate and .375 M H_2O_2 in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate and 5% t-butanol.

b. This reaction contained 1.56 x 10^{-4} M sodium salicylate.

c. Oxalate components supersaturated with CPPO (.34 M and .40 M respectively) were used in these experiments.

J. Storage Stabilities of Oxalate Components Containing 1-ClBPEA

A series of storage stability experiments were carried out with the high light capacity (over 900 lumen hour liter^{-1}) chemiluminescent systems containing 1-ClBPEA, which were optimized as described in the preceding section. The results of the stability tests, which were carried out in Teflon FEP at 75°C, are summarized in Table 32. Two concentrations of 1-ClBPEA were employed (.007 M and .008 M in the chemiluminescent reaction) and the effect of the antioxidant 2,6-di-t-butyl-p-cresol (DBPC) on the stability of each formulation was also determined. Light capacities over 600 lumen hours liter^{-1} were obtained after 90 days at 75°C from formulations which contained the antioxidant 2 6-di-t-butyl-p-cresol (DBPC). Appreciably lower light outputs (light capacities 371 and 448) were observed from the oxalate components stored without the antioxidant. The effect of the antioxidant is also apparent from the amount of 1-ClBPEA remaining after the 90 day period (67-68% remained without DBPC, while 88-89% remained with DBPC).

A series of storage stability experiments was carried out on three formulations containing TMATS to determine if this catalyst could overcome the deterioration of oxalate components stored at 100°F and 90% relative humidity in polyethylene and to determine the storage stability in polyethylene protected from moisture. The results summarized in Table 33 indicate that a slight reduction in light output is evident after 10 days at high humidity with all three concentrations of TMATS. The two higher TMATS concentrations gave better performance after 20 days at 100°F, 90% relative humidity than the long-lived formulation, but slight induction periods were evident in both of these samples. All three formulations showed severe reductions in performance after 30 days at high humidity. Satisfactory performance was observed for all three formulations stored for 30 days at 25°C and 50°C in polyethylene.

Table 32

STORAGE STABILITIES OF OXALATE COMPONENTS CONTAINING CPPO AND 1-ClBPEA AT 75°C IN TEFLON F. E. P.[a]

Oxalate Component 1-ClBPEA $M \times 10^3$	DBPC	Days Stored	% 1-ClBPEA Remaining[b]	% of Initial Lt. Cap.	Lt. Cap.[c]	Q. Y. $\times 10^2$	T.75	Intensity (Ft. Lambert cm^{-1}) vs. Time (Min) 2	10	30	60	90	120	180	240
10.67	None	0	--	--	891	13.9	110	68.5	64.7	50.0	31.6	21.2	14.1	5.9	2.9
		14	--	95	845	13.2	98	74.6	66.6	48.1	31.8	19.8	12.3	4.9	2.4
		28	87	85	757	11.8	77	79.7	72.8	48.9	28.9	15.0	8.1	3.3	1.7
		42	87	77	689	10.8	84	77.4	71.5	43.3	21.5	12.4	7.6	3.1	1.7
		60	71	62	555	8.67	83	70.2	45.0	34.1	21.5	11.4	6.3	2.6	1.3
		90	67	42	371	5.80	127	31.3	23.6	18.3	12.5	8.9	5.8	3.0	1.6
10.67	.001 M	0	--	--	940	14.7	105	71.1	70.8	53.3	34.0	23.4	15.3	6.0	2.8
		14	--	98	918	14.3	97	78.9	74.0	52.8	34.2	21.4	12.9	5.1	2.5
		28	90	90	842	13.2	71	94.1	84.6	56.7	33.0	16.6	8.3	3.0	1.4
		42	97	86	807	12.6	75	96.0	87.5	52.3	26.7	14.9	8.4	3.1	1.6
		60	87	78	736	11.5	70	93.7	63.9	47.6	33.0	15.0	7.0	2.3	1.0
		90	89	64	604	9.44	108	55.1	42.7	31.4	20.5	15.6	10.3	4.4	2.0
9.33	None	0	--	--	893	13.9	108	70.6	66.2	49.8	33.1	20.1	13.1	5.6	2.9
		14	--	98	879	13.7	100	81.8	71.8	50.7	31.2	18.7	11.9	5.1	2.6
		28	88	85	758	11.8	80	83.2	73.4	48.3	26.7	14.5	8.1	3.5	1.9
		42	90	83	746	11.7	88	84.1	77.3	46.0	22.5	13.1	8.2	3.6	2.1
		60	80	72	645	10.1	91	55.9	50.1	40.2	25.5	13.7	7.7	3.5	1.8
		90	68	50	448	6.99	122	38.5	30.5	22.8	15.0	10.3	6.6	3.3	1.8
9.33	.001 M	0	--	--	929	14.5	103	73.1	72.3	53.4	33.2	22.1	14.0	5.5	2.8
		14	--	99	916	14.3	93	83.0	78.4	54.0	33.8	20.5	12.3	4.8	2.4
		28	95	90	840	13.1	73	96.4	86.0	55.7	31.1	16.0	8.3	3.3	1.7
		42	102	89	824	12.9	73	102.0	94.1	52.4	25.6	14.0	8.2	3.2	1.6
		60	89	83	774	12.1	80	71.7	64.7	50.5	32.5	17.0	8.8	3.3	1.6
		90	88	71	661	10.2	111	61.0	48.2	35.0	22.0	16.0	10.5	4.7	2.3

a. Stored oxalate components contained .28 M bis(2,4,5-trichloro-6-carbopentoxyphenyl) oxalate (CPPO) and the indicated concentrations of 1-chloro-9,10-bis(phenylethynyl) anthracene (1-ClBPEA) and 2,6-di-t-butyl-p-cresol (DBPC) in dibutyl phthalate. Chemiluminescent reactions were run against a single sample of the activator component (3 vols. oxalate/1 vol. of activator) which contained .002 M sodium salicylate and 1.5 M H_2O_2 in a solvent of 80% (by vol.) of dimethyl phthalate, 20% t-butanol.

b. As determined by absorption spectrum.

c. Light capacity in lumen hours $liter^{-1}$.

d. Quantum yield in einsteins $mole^{-1}$.

Table 33

STORAGE STABILITY OF CHEMILUMINESCENT SYSTEMS CONTAINING TETRAMETHYLAMMONIUM 3,5,6-TRICHLOROSALICYLATE (TMATS)[a]

Conc. TMATS M x 10^4	Storage Conditions	Days Stored	Intensity (Ft. Lamberts cm^{-1}) vs. Time (Hours)										
			0	1	2	3	4	6	8	10	12	14	16
1.0	None	0	44.5	11.9	10.2	8.6	7.6	5.9	4.7	3.9	3.1	2.5	2.0
1.0	100°F, 90% R.H.	10	12.2	9.9	8.5	7.0	5.8	4.7	3.9	3.3	2.9	2.2	1.7
1.0		20	0.3	0.1	1.1	1.0	0.8	0.6	0.6	0.5	0.4	0.3	0.3
1.0		30	0.7	0.9	1.0	1.1	1.1	0.9	0.9	0.9	0.8	0.7	0.7
1.0	50°C, 0% R.H.[b]	30	76.9	10.2	8.7	7.6	6.4	5.6	4.2	3.4	3.1	2.6	---
1.0	25°C, 0% R.H.[b]	30	29.3	10.5	8.5	8.3	7.2	5.9	4.8	4.4	3.7	3.0	2.3
1.56	100°F, 90% R.H.	0	56.9	15.3	12.7	10.5	8.8	6.4	4.6	2.9	1.8	1.2	0.8
1.56		10	46.1	12.6	10.4	8.6	7.2	5.7	4.7	3.4	2.0	1.2	0.8
1.56		20	3.4	9.9	8.0	6.7	5.8	5.3	3.6	1.7	0.9	6.1	0.4
1.56		30	6.9	1.1	1.2	1.3	1.2	1.1	0.9	0.9	0.7	0.7	0.7
1.56	50°C, 0% R.H.[b]	30	93.4	13.8	11.5	9.7	8.1	6.5	5.2	3.8	2.7	1.8	---
1.56	25°C, 0% R.H.[b]	30	51.6	14.6	11.3	10.6	8.9	7.4	4.9	3.4	2.3	1.5	1.1
5.0	100°F, 90% R.H.	0	93.9	28.2	18.6	11.1	5.5	1.1	0.4	---	---	---	---
5.0		10	68.9	22.5	16.2	10.9	6.1	1.4	0.5	---	---	---	---
5.0		20	4.6	20.2	18.0	9.1	3.1	0.6	0.4	---	---	---	---
5.0		30	6.5	4.2	4.4	3.8	3.2	2.5	1.8	1.5	1.1	1.1	0.9
5.0	50°C, 0% R.H.[b]	30	177.0	25.4	17.0	11.4	6.2	1.6	0.8	---	---	---	---
5.0	25°C, 0% R.H.[b]	30	102.0	28.4	17.4	11.8	6.9	2.2	0.8	---	---	---	---

a. Oxalate component (7.5 ml) contained 0.28 M bis(2,4,5-trichloro-6-carbopentoxyphenyl) oxalate (CPPO), .00933 M 1-chloro-9,10-bis(phenylethynyl)anthracene (1-ClBPEA) and was sealed in a 6-inch polyethylene lightstick which contained an N51A glass pod with 1.5 H_2O_2 and the TMATS catalyst in 80 volume % dibutyl phthalate, 20 volume % t-butyl alcohol (2.5 ml.).

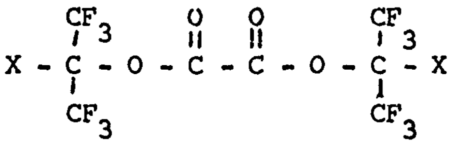
b. These lightsticks were wrapped with a moisture proof aluminum polyethylene laminate.

V. OXALATE SYNTHESIS AND EVALUATION

A. Design and Synthesis of New Oxalate Esters

1. Derivatives of Hexafluoroacetone

Aliphatic oxalate esters have the potential advantages of high solubility and low molecular weight. The most efficient aliphatic oxalate yet prepared[3] is bis(2-trichloromethyl-1,1,1,3,3,3-hexafluoro-2-propyl)oxalate (TCHFO). This compound is highly reactive towards hydrogen peroxide but suffers concentration quenching above 0.10 M.



$$\mathrm{X-\underset{CF_3}{\overset{CF_3}{C}}-O-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-O-\underset{CF_3}{\overset{CF_3}{C}}-X}$$

1a X = CCl_3 ; TCHFO

1b X = CN ; CNHFO

1c X = C ≡ C-Ph; PEHFO

We therefore sought to modify the structure of TCHFO to increase the resistance to concentration quenching and possibly change the reactivity towards hydrogen peroxide.

The reactivity of an oxalate towards nucleophilic displacement by hydrogen peroxide generally increases with the acidity of the leaving group.[1] Knunyants[15] has established that for a series of fluorinated alcohols a linear reaction exists between the sum of the Taft polar substituent constants[15], $\sum \sigma^*$, and pKa. The acidities of several derivatives of 1,1,1,3,3,3-hexafluoro-2-propanol were estimated and the results summarized in Table 34.

Table 34

Acidities of Fluorinated Alcohols, X $(CF_3)_2COH$

X	σ^*	$\sum\sigma^*$	pKa Calcd.[a]	pKa Found	Derived Oxalate
CF_3	2.60	7.80	5.4	5.2[17]	-----
CCl_3	2.65	7.85	5.4	5.1[17]	TCHFO
C ≡ C-Ph	1.35	6.55	7.2	7.8-7.9[14]	PEHFO
CN	3.64	8.84	3.9	Not Measured	CNHFO

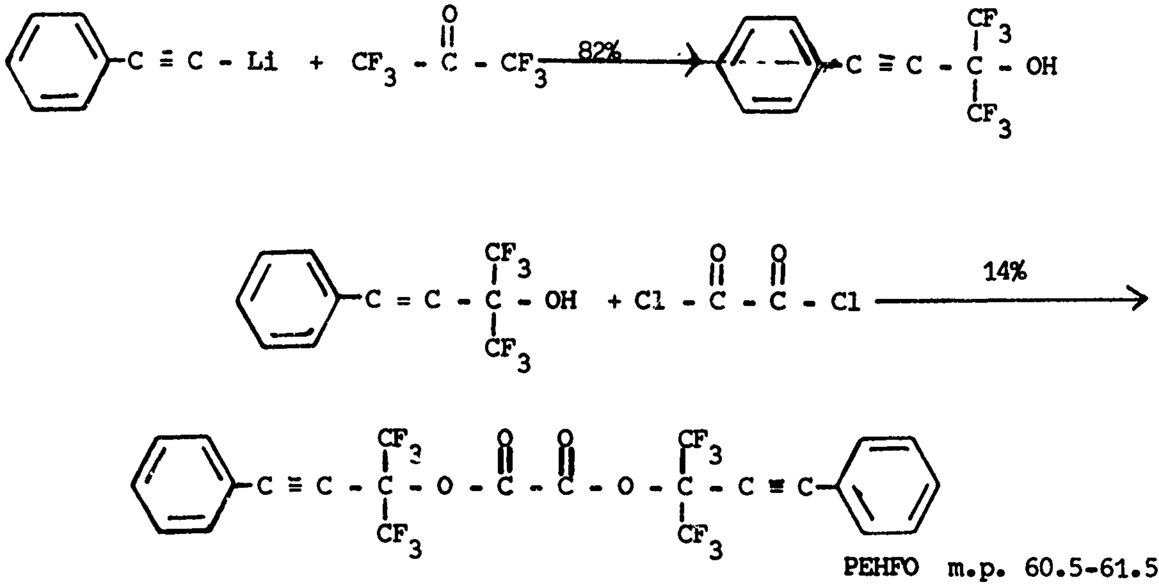
a. Calculated by the following equation[15]: $pKa = 1.44\sum\sigma^* + 16.67$.

The pKa, while a general guide to ascertaining reactivity, is not the only factor operating. For example, on the basis of pKa alone one would predict TCHFO would be about as reactive as CPPO (pKa's of the products are 5.45 and 5.1 respectively). However, CPPO requires basic catalysis and even with catalysis its reaction rate remains slower than TCHFO. With this in mind we selected PEHFO (X = C ≡ C-Ph) and CNHFO (X = CN) as potential chemiluminescent materials. We expected PEHFO to react somewhat slower than TCHFO and the cyano derivative to react faster.

The synthesis of PEHFO was accomplished[18] according to the route outlined in Chart V.

Chart V

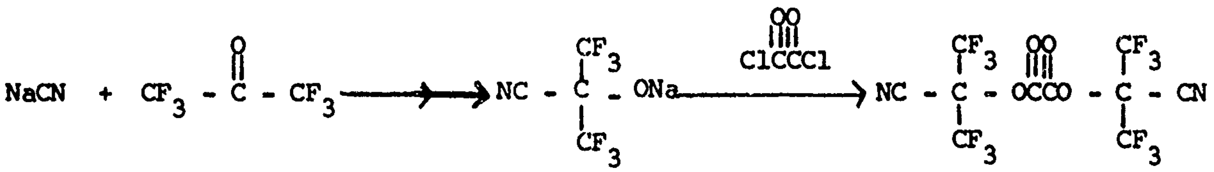
Synthesis of Bis(2-Phenylethynyl-1,1,1,3,3,3-Hexafluoro-2-Propyl) Oxalate (PEHFO)



PEHFO m.p. 60.5-61.5°C

The oxalate ester (PEHFO) is highly soluble in dibutyl phthalate (solution up to at least 1 M can be prepared) and can be purified by recrystallization from petroleum ether. The chemiluminescent performance of PEHFO is summarized in Section V-2. The data indicated that this compound is inherently efficient at .01 M but that concentration quenching substantially reduces the efficiency at .10 M. Although PEHFO is not suitable for a practical chemical lighting system, it does indicate that a solid oxalate and high solubility in dibutyl phthalate are not mutually exclusive.

The cyanohydrin of hexafluoroacetone has not been characterized. However, alkylations of the sodium cyanide-hexafluoroacetone adduct have been reported. The oxalate ester, CNHFO, was therefore prepared (in 28% yield) by treatment of this adduct with oxalyl chloride.[8] The chemiluminescent performance of this oxalate is summarized in Section V-2.

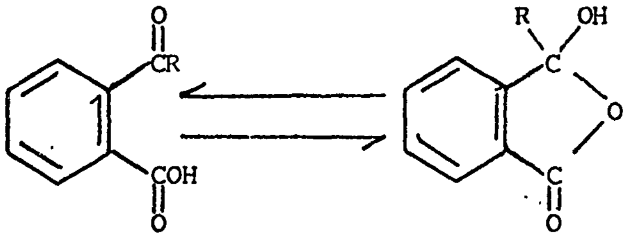


CNHFO
m.p. 113-114.5°C

The efficiency was only about half of the efficiency obtained with TCHFO, and the solubility in dibutyl phthalate was low (.04 M maximum).

2. Derivatives of Phthaldehydic Acid

Phthaldehydic acid (2 a,b) exists as an equilibrium mixture of cyclic (87%) and open chain (13%) tautomers. The cyclic form, 2b, is reported[19] to have an acidic hydroxyl function (pKa = 4.53).



2a R = H
2c R = CH_3

2b R = H
2d R = CH_3

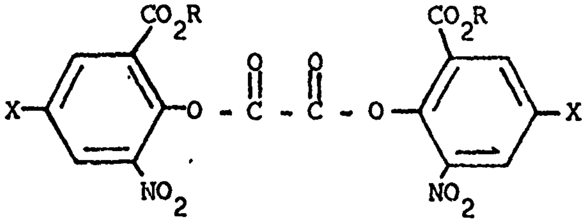
On the basis of the literature[19,20,21] we thought that the oxalate ester derived from 2b might be an efficient chemiluminescent material, since the anion of 2b should be a good leaving group in a nucleophilic displacement. Moreover, addition of phthaldehydic acid to a CPPO chemiluminescent reaction did not produce noticeable quenching.

Treatment of phthaldehydic acid with oxalyl chloride and pyridine gave a solid, m.p. 239-240 dec. Elemental analysis together with infrared spectral evidence suggested the product was the desired oxalate ester of the cyclic form, 2b. The oxalate proved to be highly insoluble in most organic solvents (sol. in dibutyl phthalate $< 5 \times 10^{-4}$ M), which precluded a normal nmr analysis.

We attempted to improve the solubility by preparing an oxalate derived from the cyclic form of o-acetylbenzoic acid (2d). The oxalate could not be purified to permit quantitative evaluation of its chemiluminescence, but the crude product did give light emission on treatment with H_2O_2 and a fluorescer.

3. Nitrosalicylic Acid Derivatives

The most efficient oxalate ester now known is bis(2,4-dinitrophenyl) oxalate (DNPO), which gives a 23% quantum yield[22] at .001 M concentration. However, DNPO is not suitable for a practical chemical lighting system because of low solubility, poor storage stability and serious concentration quenching. Since introduction of another carboalkoxy group was found to improve solubility and substantially decrease concentration quenching in bis-trichlorophenyl oxalates,[2,3] a series of nitro substituted carboalkoxyphenyl oxalates was prepared. The oxalate esters indicated in formula 3 were prepared as typical representatives of the series.



3a X = NO_2, R = $n\text{-}C_4H_9$ (DNCPO)

3b X = Cl, R = $n\text{-}C_5H_{11}$ (NCPO)

Oxalate DNCPO had been prepared previously[2] by treatment of butyl 3,5-dinitro-salicylate with oxalyl chloride. However, its chemiluminescence performance could not be determined because too little of the oxalate was obtained. In the present work sufficient quantities for evaluation were achieved. Oxalate NCPO was prepared in a similar manner by reaction of pentyl 3-nitro-5-chlorosalicylate with oxalyl chloride. Recrystallization from hexane afforded the pure NCPO, m.p. 85.5-87. Preparation of the starting material 3-nitro-5-chloro salicylic acid was accomplished by nitration of 5-chlorosalicylic acid with a 25% excess of 10% aqueous nitric acid at 70°. The use of more drastic nitration conditions caused decarboxylation and the formation of large quantities of 2,6-nitro-4-chlorophenol.

B. Chemiluminescent Performance of New Oxalates

1. Derivatives of Hexafluoroacetone

The soluble, efficient aliphatic oxalate ester, bis(2-trichloromethyl-1,1,1,3,3,3-hexafluoro-2-propyl)oxalate (TCHFO), has been evaluated in chemiluminescent systems containing 1,8-DCBPEA and the results are summarized in Table 35. Since this oxalate has been shown to react very rapidly with hydrogen peroxide in the absence of a catalyst, the effect of addition of two acids on the decay curve shape was explored. Only minor effects were evident by the addition of acetic acid at the four oxalate concentrations studied. Trifluoroacetic acid, however, provided a marked effect at .10 M TCHFO causing a three fold increase in the three quarter lifetime and providing a brightness of 1.7 foot lamberts cm^{-1} after an hour.

As indicated by the results summarized in Table 36, the use of 1-ClBPEA as the fluorescer in the TCHFO reactions gives more than a 40% increase in light capacity at the .10 M oxalate concentration compared to a similar system formulated with 1,8-DCBPEA. The 14% quantum yield obtained is particularly encouraging since it indicates the basic hexafluoro-2-propyl substrate may be highly effective at higher concentration with alternative groups substituted on the oxalate.

The chemiluminescent performance of two such oxalates is summarized in Table 37. Oxalate PEHFO reacted somewhat slowly with H_2O_2 and severe concentration quenching was observed upon increasing the concentration from 0.01 to 0.10 M (quantum yield decreased from 5.7% to 0.35%). The cyano compound reacted more rapidly (T.75 $<$ 2 minutes), but the efficiency at the solubility limit (.03 M) was only about half of that found with TCHFO.

2. Nitro Salicylic Acid Derivatives

The chemiluminescent performance of NCPO and DNCPO is summarized in Table 38. The oxalate NCPO is fairly efficient at .01 M concentration (10% quantum yield), but suffers severe quenching when the ester concentration is increased ten fold. Relatively high catalyst concentration is required for a reasonable lifetime

TABLE 35

CHEMILUMINESCENT PERFORMANCE OF TCHFO WITH 1,8-DCBPEA[a]

TCHFO M	ACID M	Q. Y. x 10^2	LT. CAP.	T.75	INTENSITY (FT. LMBT. CM^{-1}) VERSUS TIME (MINUTE)								
					0	2	5	10	20	30	40	50	60
.05	------	6.72	96.2	2.5	421.	123.	18.9	0.72	----	-----	----	----	----
.05	Acetic	7.82	112.	2.0	1096.	91.6	23.1	0.39	----	-----	----	----	----
.10	------	10.0	287	8.2	908.	204.	98.6	44.3	14.0	3.0	0.3	----	----
.10	Acetic	8.36	239	9.8	951.	154.	70.8	33.6	14.3	6.0	1.9	----	----
.10	------	10.2	292	7.6	227.	189.	193	51.2	8.7	1.1	0.3	0.1	----
.10	TFA (4 x 10^{-4})	9.66	276	22.0	226.	106.	69.2	51.8	30.2	18.0	8.9	3.9	1.7
.20	------	0.91	52.1	0.7	690.	4.5	0.22	----	----	-----	----	----	----
.20	Acetic	1.25	71.4	0.8	690.	10.1	0.22	----	----	-----	----	----	----

a. Chemiluminescent reactions contained the indicated concentrations of bis-(2-trichloromethyl-1,1,1,3,3,3-hexafluoropropyl)oxalate (TCHFO), 5.67 x 10^{-3} M 1,8-dichloro-9,10-bis(phenylethynyl)anthracene (1,8-DCBPEA) and 0.375 M H_2O_2 in a solvent of 75% (volume) dibutyl phthalate, 20% dimethyl phthalate and 5% t-butanol. TFA is trifluoroacetic acid.

Table 36

CHEMILUMINESCENT PERFORMANCE OF TCHFO WITH 1-ClBPEA[a]

Conc. TCHFO	Q. Y.[b] x 10^2	Lt. Cap.[c]	T-75[d]	Intensity (Ft. Lamberts cm^{-1}) vs. Time (Min.)						
				0	2	10	30	60	90	120
.10	14.2.	419	37	241	122	55.4	29.9	11.9	2.0	0.5
.20	1.95	111	8.9	332	68.0	27.4	0.5	----	---	---

a. Chemiluminescent reactions contained the indicated concentrations of bis(2-trichloromethyl-1,1,1,3,3,3-hexafluoro-2-propyl)oxalate (TCHFO), .008 M 1-chloro-9,10-bis-(phenylethynyl)anthracene (1-ClBPEA), .375 M H_2O_2 and 1 x 10^{-4} M trifluoroacetic acid in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol.

b. Quantum yield in einsteins $mole^{-1}$.

c. Light capacity in lumen hours $liter^{-1}$.

d. Time required for emission of 75% of the total light.

Table 37

CHEMILUMINESCENCE PERFORMANCE OF NEW OXALATES[a]

Fluorescer	Oxalate Conc. M	Catalyst M x 10^4	Q. Y. x 10^2	Lt. Cap.	T.75	Intensity (Ft. Lbt. cm^{-1}) Versus Time (Minutes) 0	2	10	30	60	90	120
BPEA	PEHFO .01	None	-----[c]	----	---	0.3	0.4	0.4	1.1	0.9	0.7	---
BPEA	PEHFO .01	NaSal 1.56	6.72	18.4	33	38.9	5.9	2.1	1.1	0.4	0.1	0.1
BPEA	PEHFO .10	NaSal 1.56	0.35	9.5	43	3.6	2.5	1.3	0.6	0.2	0.1	---
1-ClBPEA	PEHFO .01	NaSal 1.56	9.78	29.3	59	24.7	7.4	2.7	1.7	0.9	0.5	0.3
1-ClBPEA	PEHFO .10	NaSal 1.56	0.33	10.0	81	0.3	0.4	0.8	0.7	0.5	0.2	0.1
1,8-DCBPEA	CNHFO .03	None	4.81	41.4	1.7	287	35.5	0.2	---	---	---	---
1,8-DCBPEA	CNHFO .03	TFA 4.0	5.08	43.6	1.9	217	41.5	0.4	---	---	---	---

a. H_2O_2 concentration 0.375 M. Concentration of 9,10-bis(phenylethynyl)anthracene (BPEA) was 2.25 x 10^{-3} M and 1-chloro-9,10-bis(phenylethynyl)anthracene (1-ClBPEA) was 5 x 10^{-3} M. NaSal is sodium salicylate. TFA is trifluoroacetic acid. Solvent system: 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol.

b. Oxalates used: bis(2-phenylethynyl)-1,1,1,3,3,3-hexafluoro-2-propyl)oxalate (PEHFO) and bis(2-cyano-1,1,1,3,3,3-hexafluoro-2-propyl)oxalate.

c. Extrapolated portion of the total decay area was too large for accurate quantum yield and light capacity determination.

TABLE 38

CHEMILUMINESCENT PERFORMANCE OF OXALATES DERIVED FROM NITROSALICYLATES

								INTENSITY (FT. LBT. CM^{-1}) VS. TIME (MIN.)							
OXALATE	M	NaSal M x 10^4	FLUORESCER	M x 10^3	Q. Y. x 10^2	LT. CAP.	T.75	0	2	10	30	60	90	120	180
NCPO	.10	1.56	1-ClBPEA	7.0	b	----	--	16.7	13.3	3.5	1.0	0.5	0.3	0.3	0.2
NCPO	.01	5.0	1-ClBPEA	7.0	10.8	34.5	26	22.7	16.2	5.3	1.4	0.3	0.1	---	---
NCPO	.01	5.0	1-ClBPEA	7.0	9.62	30.6	17	28.0	16.4	5.2	1.2	0.3	0.1	---	---
DNCPO	.10	None	BPEA	2.25	0.61	18.3	44	4.6	10.1	2.3	0.6	0.3	0.2	---	---

a. Chemiluminescent reactions contained the indicated concentrations of bis-(2-nitro-4-chloro-6-carbopentoxyphenyl)oxalate (NCPO), bis(2,4-dinitro-6-carbobutoxyphenyl)oxalate (DNCPO), 1-chloro-9,10-bis(phenylethynyl)anthracene (1-ClBPEA), 9,10-bis(phenylethynyl)anthracene (BPEA) and sodium salicylate (NaSal). H_2O_2 concentration was 0.375 M.

b. Extrapolated portion of the total decay area was too large for accurate quantum yield and light capacity determination.

at .01 M NCPO, but the slow reaction rate of DNCPO is somewhat surprising. A rapid reaction is observed with bis(2,4-dinitrophenyl)oxalate in the absence of catalyst, and one would normally expect the addition of carboalkoxy group to increase the acidity of the leaving group and increase the rate of nucleophilic displacement by H_2O_2. The opposite result was found, however, indicating again that other factors, possibility steric effects, contribute to the rate effect.

VI. STORAGE STABILITY OF BPEA OXALATE COMPONENTS

A. Effect of Storage Conditions on Development of Induction Periods

Some batches of first generation oxalate component (.133 M CPPO and .003 M BPEA in dibutyl phthalate) develop induction periods after 10 days storage in polyethylene lightsticks at 100°F and 90% relative humidity. Other batches require 20 to 30 days to develop the induction period while some others never develop the induction period but merely lose lifetime during 30 days storage in the humidity oven. We carried out a series of experiments in an effort to define the causes of this induction period.

It is known that water under certain circumstances can produce the induction period; polyethylene lightsticks stored in a humidity oven develop the induction period while identical lightsticks stored dry do not. Heating an oxalate component having an induction period at 75°C restores the initial performance temporarily, but the induction period generally reoccurs even in room temperature storage. The addition of sodium salicylate, a weak base, or weak acids (phthalic, acetic) does not cause the formation of the induction period in humidity oven tests. Strong acids such as oxalic acid quench the chemiluminescent reaction from the time of addition. In general, the causes of the induction period could be one or a combination of the following: water, polyethylene, oxygen and unknown contaminants.

Two Cyanamid production batches of the oxalate component were employed in this study: batch 6031 (did not develop an induction period in humidity storage) and batch 6030 (developed an induction period after 10 days in the humidity oven).

These oxalate components were stored as received and with 0.02 M water added under four sets of conditions; (1) in polyethylene lightsticks at 100°F, 90% relative humidity, (2) in polyethylene lightsticks at 100°F sealed in a glass tube under nitrogen, (3) in polyethylene lightsticks at 100°F sealed in a glass tube under oxygen, and (4) in sealed N51A glass ampoules at 100°F. The stored components were evaluated against a single lot of activator component which was kept at room temperature in a Teflon FEP bottle. All the lightsticks contained a filled N51A glass pod of activator component which was used where indicated in the tables.

Table 39 summarizes the data obtained with the typical "good" batch, 6031. In the humidity storage test the presence of water had no significant effect on the performance. No induction period was apparent after 30 days and the initial intensity values actually increased with storage. The presence of water had no effect in storage under nitrogen, although the light capacity was somewhat higher than the samples exposed to humidity. A comparison of the samples stored in oxygen versus nitrogen revealed a slightly lower light output from oxygen storage but no indications of any induction period. Again, the presence of water at 0.02 M made little difference. Good performance was obtained from both oxalate components stored in the N51A ampoules.

Table 40 summarizes a similar set of experiments carried out on oxalate component batch 6030 which in an earlier test had been shown to develop an induction period after 10 days storage at high humidity. In experiments carried out with unstored activator component, after 30 days in the humidity oven the light capacity fell to about 200 lumen hours liter^{-1} but no induction period was evident. The pattern of the results in the other tests paralleled the data from batch 6031. The samples under nitrogen gave slightly higher light capacities than those stored under oxygen and good performance was obtained in the N51A ampoules. Again, the presence of water in these samples did not make any significant difference. Since these results were contrary to those obtained previously on batch 6030, we determined the effect of the stored activator component on the samples of oxalate which had been stored 30 days under each set of conditions. Induction periods now became apparent in both of the samples which had been stored in the humidity oven. Iodometric titration indicated no loss of peroxide in the activator, suggesting that the combination of a trace of acid in the activator and a partially deteriorated oxalate component was responsible for the induction period.

An extensive set of experiments was set up to explore the possibility that the combination of partially deteriorated oxalate and activator components was responsible for formation of an induction period. The data from this set of storage stability experiments is summarized in Table 41. After 10 days storage the initial intensity values increase with a corresponding decrease in the 10 and 30 minute intensities resulting in a small loss in light capacity. After 20 days storage induction periods are evident in the samples with batch 6030 being the most pronounced, but no large decrease in light capacity is noted. At the 30 day point, however, the loss in early brightness in batch 6031 particularly becomes quite pronounced. The induction period observed in the sticks from batch 6031 is considerably longer than in batch 6030 although the latter sample has a slightly lower light capacity. We conclude from this set of experiments that induction periods can be produced in humidity-stored lightsticks after 20 days, but these induction periods do not become serious until 30 days storage at 100°F, 90% relative humidity. In this series of experiments, no significant difference was noted in the use of unstored activator versus activator which had been stored in the N51A glass pod within the lightstick.

Data summarized in Tables 39 and 40 indicated that the addition of .02 M water to the oxalate component did not cause formation of an induction period during 30 days storage at 100°F. Subsequently, it was determined that .11 M (0.20%) water permeates the polyethylene lightstick at 100°F, 90% relative humidity in 10 days. A series of experiments using 0.20 M (0.36%) and 0.28 M (0.50%) water added to the oxalate component were set up in N51A glass pods in an effort to approximate the humidity storage conditions. Table 42 summarizes the results of these experiments. At the higher water concentration, batch 6030 gave very low light output immediately. Batch 6031, on the other hand, initially gave an induction period which disappeared after 10 days at 100°F. This might be due to the decomposition of the oxalic half-ester at 100°F regenerating CPPO as well as a reduction of the concentration of the half-ester, a probable acidic quencher, via decomposition. At the 0.20 M water concentration no induction periods were produced up to 21 days at 100°F, although significant reductions in light capacity were observed. The rather large difference in the effect of water at 0.28 M versus 0.20 M seems surprising. It is possible that water may separate as a liquid phase under these conditions, and that extraction of catalyst by the aqueous phase was responsible for the results.

A series of experiments was carried out to determine whether a contaminant in the polyethylene lightstick might contribute to the cause of the induction period. Table 43 summarizes the effect of heating the empty lightstick in air and extracting the empty stick with dibutyl phthalate. Neither treatment made any large difference in the humidity stability of the oxalate component, although the light capacity of batch 6030 in the lightstick which had been heated was slightly lower (174) than the other samples. The humidity stability of an oxalate component prepared from the dibutyl phthalate extract of the lightsticks was also satisfactory. Table 44 summarizes the effect of the addition of 0.02 M pentyl 3,5,6-trichlorosalicylate (PTCS) on the humidity stability of oxalate batches 6030 and 6031. The loss in light capacity was about the same as in the untreated samples, but a slight induction period was evident in both PTCS-treated samples after the 30 day period.

Mr. H. Richter[23] has indicated that formation of induction periods can be minimized by treatment of the oxalate component with silica gel. Table 45 summarizes the humidity stability of oxalate component 6030 treated with increasing amounts of silica gel. Each solution was stirred at room temperature with the

Table 39

OXALATE COMPONENT BATCH 6031 STABILITY TEST SERIES[a,b]

Stored Component	Storage Conditions	Days Stored	Lt. Cap.[d]	T-75[e]	Intensity (Ft. Lbt. cm^{-1}) vs. Time (Minutes)							
					0	2	10	30	60	90	120	180
Batch 6031		0	288	92	34.8	32.4	26.8	18.2	9.1	5.0	3.1	1.6
		10	246	119	59.3	23.0	16.4	12.4	8.4	5.6	3.8	2.0
		30	234	159	79.8	24.9	13.8	9.7	6.9	4.9	3.4	2.0
Batch 6031 + .02 M H_2O		0	268	93	32.9	30.6	25.0	16.6	8.4	4.7	3.0	1.5
		10	226	99	67.7	25.9	17.7	12.6	7.7	4.8	3.0	1.6
		30	226	135	83.1	25.5	14.2	10.0	7.2	5.0	3.3	1.8
Batch 6031		0	299	115	63.4	26.4	19.4	15.4	10.8	7.0	4.6	2.2
		10	285	90	61.2	31.1	26.9	18.3	8.5	4.6	3.0	1.5
		30	278	129	56.5	22.2	17.1	14.1	10.1	6.4	4.1	2.1
Batch 6031 + .02 M H_2O		0	288	122	60.5	24.6	18.2	14.3	10.1	6.8	4.5	2.3
		10	293	87	75.2	35.6	28.2	18.5	8.6	4.7	3.0	1.6
		30	266	122	66.2	24.5	17.8	13.9	9.5	5.7	3.7	1.9
Batch 6031		0	296	116	56.6	25.7	19.2	15.3	10.8	6.9	4.5	2.2
		10	247	113	50.5	23.2	16.3	13.0	8.4	5.9	4.0	1.9
		30	231	128	50.7	18.7	13.3	11.0	8.2	5.5	3.8	2.1
Batch 6031 + .02 M H_2O		0	286	121	58.2	24.7	18.1	14.3	10.2	6.8	4.5	2.3
		10	254	112	56.2	24.8	17.1	13.5	8.5	5.9	3.9	1.9
		30	224	112	59.6	20.8	14.7	11.7	8.2	5.1	3.4	1.8
Batch 6031		0	279	115	52.0	24.7	19.0	14.6	9.9	6.4	4.1	2.0
		10	292	84	67.7	34.0	27.5	18.5	9.6	5.4	3.5	1.6
		30	265	110	66.9	26.3	18.3	13.8	9.3	6.5	3.9	2.0
Batch 6031 + .02 M H_2O		0	268	93	32.9	30.6	25.0	16.6	8.4	4.7	3.0	1.5
			280	80	71.2	34.9	26.8	17.6	9.3	4.9	3.2	1.5
		30	260	108	77.2	27.7	18.7	13.6	9.0	6.2	3.9	2.0

Footnotes on page 125.

Table 40

OXALATE COMPONENT BATCH 6030 STABILITY TEST SERIES[a,b]

Stored Component	Storage Conditions	Days Stored	% H_2O_2[g] of Theory	Lt. Cap.[d]	T-75[e]	Intensity (Ft. Lbt. cm^{-1}) versus Time (Minutes)							
						0	2	10	30	60	90	120	180
6030	Stick at 90% R.H., 100°F	0[*]	---	270	96	59.6	25.3	18.9	15.4	10.6	6.7	4.4	2.2
		11	---	260	142	38.9	21.4	15.1	12.3	8.9	6.0	4.0	2.2
		30	---	202	123	78.9	23.5	12.5	8.8	6.8	4.8	3.2	1.6
		30[f]	101	201	114	5.2	15.6	11.9	10.2	8.4	5.5	3.5	1.6
6030 + .02 M H_2O	Stick at 90% R.H., 100°F	0[**]	---	293	125	61.4	24.9	18.4	15.1	10.3	6.5	4.2	2.2
		11	---	267	141	22.0	22.1	16.1	12.6	9.2	6.3	4.2	2.3
		30	---	201	125	32.8	22.8	12.4	9.0	7.0	5.0	3.3	1.7
		30[f]	103	205	111	2.3	11.6	12.0	10.7	9.1	5.9	3.7	1.6
6030	Stick under N_2 at 100°F	0	---	263	104	62.2	24.3	17.9	14.4	9.9	6.3	4.0	2.1
		12	---	240	109	54.5	19.2	14.7	12.7	9.3	6.0	3.7	2.0
		30	---	272	131	60.3	19.4	14.3	12.4	10.3	7.0	4.5	2.2
		30[f]	102	280	103	64.0	23.1	16.7	15.5	11.9	7.0	4.3	1.9
6030 + .02 M H_2O	Stick under N_2 at 100°F	0	---	268	100	72.6	24.7	18.1	14.9	10.3	6.4	4.2	2.2
		12	---	249	110	61.2	20.8	15.4	13.2	9.3	5.9	3.8	2.0
		30	---	275	124	68.5	21.4	15.5	13.1	10.3	6.8	4.3	2.2
		30[f]	103	274	103	69.6	23.9	16.7	15.2	11.2	6.6	4.1	1.9
6030	Stick under O_2 at 100°F	0	---	270	96	59.6	25.3	18.9	15.4	10.6	6.7	4.4	2.2
		10	---	244	145	52.9	18.0	12.6	10.7	8.5	5.7	4.1	2.1
		30	---	263	118	61.2	21.0	15.8	13.3	10.0	6.2	4.0	1.9
		30[f]	102	263	107	64.6	22.0	15.8	14.6	10.5	6.3	4.0	1.9
6030 + .02 M H_2O	Stick under O_2 at 100°F	0	---	293	125	61.4	24.9	18.4	15.1	10.3	6.5	4.2	2.2
		10	---	243	138	54.7	19.5	13.5	11.2	8.5	5.5	3.9	2.0
		30	---	248	138	61.2	19.0	13.4	11.3	8.9	5.9	4.0	2.1
		30[f]	102	256	105	67.0	23.1	15.9	14.3	10.2	6.0	4.0	1.9
6030	N51A Ampoule at 100°F	0	---	270	96	59.6	25.3	18.9	15.4	10.6	6.7	4.4	2.2
		10	---	254	131	55.3	21.5	15.3	12.0	8.9	5.7	4.1	2.1
		30	---	274	112	60.6	24.0	19.0	13.9	10.0	6.5	4.2	2.0
6030 + .02 M H_2O	N51A Ampoule at 100°F	0	---	293	125	61.4	24.9	18.4	15.1	10.3	6.5	4.2	2.2
		10	---	259	126	65.6	23.0	16.2	12.6	8.9	5.6	4.0	2.0
		30	---	272	127	72.3	24.8	17.5	13.0	9.2	6.0	3.9	2.1

[*] This sample contained 0.03% H_2O (by analysis).

[**] This sample contained 0.06% H_2O (by analysis).

Footnotes see page 125.

Table 41

STORAGE STABILITY OF BPEA OXALATE[a,b] COMPONENT IN LIGHTSTICKS AT 100°F AND 90% R.H.

OXALATE BATCH NO.	ACTIVATOR*	DAYS** STORED	LT. CAP.[d]	T.75[e]	Intensity (Ft. Lmbt. cm^{-1}) vs. Time (Minutes)							
					0	2	10	30	60	90	120	180
6030	Unstored	0	271	141	60.4	22.0	15.9	12.8	6.0	4.0	2.2	1.4
	Stored	0	259	93	61.0	26.3	19.5	15.4	9.9	5.5	3.5	1.8
	Unstored	10	231	127	79.3	22.6	13.6	10.3	7.5	5.6	3.5	1.8
	Stored	10	241	114	84.9	24.6	15.2	11.4	8.3	6.6	4.0	2.0
	Unstored	20	220	145	6.1	15.6	13.1	9.7	7.9	5.6	3.9	2.0
	Stored	20	213	125	5.6	14.5	12.6	10.0	8.0	5.7	4.1	2.1
	Unstored	30	166	108	----	19.1	11.9	8.4	6.6	4.5	2.9	1.3
	Stored	30	172	105	----	11.5	11.1	9.3	7.4	4.9	3.2	1.3
6031	Unstored	0	257	129	62.2	24.6	17.3	12.2	8.3	5.7	3.9	2.1
	Stored	0	265	106	62.3	28.2	20.7	14.2	8.8	5.6	3.6	1.8
	Unstored	10	233	146	73.1	22.4	14.2	10.8	7.1	5.0	3.5	2.2
	Stored	10	243	123	78.7	25.5	16.3	11.5	7.8	5.3	3.6	2.0
	Unstored	20	197	127	28.2	22.9	12.8	8.9	6.6	4.7	3.3	2.0
	Stored	20	210	146	21.4	25.7	13.3	9.4	6.5	4.7	3.4	2.0
	Unstored	30	179	131	----	2.1	4.9	7.2	7.3	7.2	5.1	2.0
	Stored	30	181	129	0.3	2.0	5.6	7.6	7.7	7.1	4.9	2.0

* Unstored activator was a single lot of activator component kept at 25°C in a Teflon F.E.P. container. Pod activator was taken from the N51A glass pod which was stored in the lightstick for the indicated period.

** The data for the 0 and 10 days storage periods is the average of four identical experiments. The 20 and 30-day data was obtained from eight identical experiments in which the highest and lowest intensity experiments were discarded and the remaining six averaged.

Other footnotes on page 125.

Table 42

EFFECT OF WATER ON STORAGE STABILITY OF BPEA OXALATE COMPONENTS IN N51A GLASS AMPOULES

OXALATE COMPONENT	H_2O M	DAYS at 100°F	LT. CAP.	T.75	Intensity (Ft. Lbt. cm^{-1}) vs. Time (Minutes)							
					0	2	10	30	60	90	120	180
6030	0	0	247	122	62.0	21.6	15.9	12.3	8.9	5.8	[illegible]	[illegible]
6030	.20	10	247	95	108.[1]	34.1	18.9	12.6	8.8	5.4	3.5	1.6
	.20	21	162	46	-----[1]	39.3	22.0	13.7	5.5	2.1	0.8	0.2
	.20	21	167	55	-----[1]	38.1	20.5	13.2	6.1	2.7	1.3	0.3
6030	.28	0	---	---	-----[1]	----	0.1	0.3	0.6	0.8	0.9	0.5
	.28	11	---	---	FAILED							
	.28	30	---	---	FAILED							
6031	0	0	257	124	68.7	23.9	16.9	12.3	8.9	6.1	4.2	2.1
6031	.20	10	220	73	108.[1]	38.0	20.4	12.7	7.9	4.5	2.5	0.9
	.20	21	184	62	-----[1]	45.7	21.0	13.2	6.8	3.4	1.6	0.5
	.20	21	177	62	-----[1]	42.8	19.8	12.7	6.6	3.2	1.6	0.5
6031	.28	0	241*	177	0.3	2.7	8.5	10.2	8.2	6.5	5.1	2.9
	.28	11	165	53	-----[1]	32.1	20.4	13.3	6.4	2.8	1.1	0.2
	.28	11	162	52	-----[1]	32.3	20.5	13.2	6.3	2.5	1.0	0.2
	.28	30	---	---	FAILED							

*The extrapolated portion amounted to 22% of the total decay area in this experiment.

Footnotes on page 125.

Table 43

STORAGE STABILITY OF OXALATE COMPONENTS IN TREATED LIGHTSTICKS[a,b]

Batch	Days 160°F at 20% R.H.	% CPPO[c]	% CPPO of Theory	% H_2O	Lt. Cap.[d]	T.75[e]	% of Initial Amt. of DPEA	Intensity (Ft. Lbt. cm^{-1}) vs. Time (Minute) 0	2	10	30	60	90	120	180
6030	0	7.8	92	.02	280	106	---	53.5	26.1	21.3	14.9	10.2	6.3	3.9	1.9
	10	7.2	85	---	272	122	99	76.3	30.7	21.1	14.9	9.2	4.5	2.8	1.5
	30	4.4	52	---	174	71	---	113.	33.7	15.9	10.0	5.3	2.8	1.6	0.7
6031	0	8.2	97	.02	277	112	---	54.1	27.4	21.2	14.2	9.7	6.1	3.9	1.9
	10	7.8	92	---	285	133	101	75.0	31.8	21.0	14.7	8.5	4.9	3.2	1.8
	30	4.9	58	---	204	110	---	110.	32.8	15.9	9.8	5.7	3.4	2.2	1.2
6030	0	7.8	92	.02	280	106	---	53.5	26.1	21.3	14.9	10.2	6.3	3.9	1.9
	10	7.2	85	---	282	122	95	87.0	31.2	21.0	15.0	8.7	4.9	3.1	1.7
	30	4.9	58	---	208	99	---	127.	34.3	16.4	10.2	6.1	3.6	2.3	1.1
6031	0	8.2	97	.02	277	112	---	54.1	27.4	21.2	14.2	9.7	6.1	3.9	1.9
	10	7.5	89	---	283	146	96	76.8	31.3	20.3	13.9	8.2	4.9	3.2	1.8
	30	5.0	59	---	210	118	---	112.	32.0	16.0	9.9	5.9	3.6	2.3	1.2
	0	8.5	100	---	286	97	---	60.9	27.4	22.9	17.8	9.7	5.4	3.3	1.8
	10	5.3	63	---	276	114	---	74.0	26.7	18.9	14.2	9.6	6.3	4.2	2.3
	30	---	---	---	215	107	---	80.7	27.6	14.6	10.5	7.3	4.9	3.4	1.7

Footnotes see Page 125.

Table 44

EFFECT OF PENTYL 3,5,6-TRICHLOROSALICYLATE (PTCS) ON STORAGE STABILITY OF OXALATE COMPONENTS[a,b]

	Days at 100°F and 90% R. H.	% CPPO (Wt)[c]	% CPPO of Theory	Lt. Cap.[d]	T-75[e]	Intensity (Ft. Lbt. cm^{-1}) versus Time (Minutes)							
						0	2	10	30	60	90	120	18
Batch 6030	0	7.1	84	282	104	82.8	32.8	21.4	14.4	9.7	6.6	3.7	1.[illegible]
+ .02 M of	10	---	--	248	94	116.	47.6	20.2	12.6	7.4	4.5	3.0	1.5
PTCS	30	---	--	185	142	12.4	18.2	10.3	8.0	6.2	4.5	3.1	1.7
Batch 6031	0	7.3	86	279	103	81.4	33.4	21.9	14.2	9.3	6.4	3.7	1.9
+ .02 M of	10	---	--	256	109	103.	40.7	19.3	12.9	7.9	5.1	3.5	1.9
PTCS	30	---	--	201	154	8.5	16.9	11.7	8.5	6.4	4.7	3.4	1.9

Footnotes on page 125.

Table 45

EFFECT OF SILICA GEL TREATMENT ON HUMIDITY STABILITY OF OXALATE COMPONENT, BATCH 6030

Silica Gel^{g} Per 100 cc of Oxalate	Days Stored 100°F, 90% R.H.	% CPPO	% CPPO of Theory	Lt. Cap.	T.75	Intensity (Ft. Lbt. cm^{-1}) versus Time (Minutes)							
						0	2	10	30	60	90	120	180
0	0	7.8	92	228	83	61.2	29.7	25.6	19.4	10.0	5.1	3.1	1.5
	3	---	--	295	118	51.8	24.8	20.2	17.3	10.2	5.6	3.4	1.7
	10	6.3	74	266	107	65.8	25.1	18.7	14.6	9.3	5.8	3.8	2.1
	30	---	---	196	110	59.1	25.1	13.4	9.5	6.5	4.4	3.0	1.5
	30^{f}	---	--	•	---	51.1	24.5	12.4	9.2	6.6	4.4	2.9	1.[illegible]
0.1	0	7.8	92	204	81	60.9	30.2	25.7	19.3	9.4	4.9	2.9	1.5
	10	6.4	70	263	110	67.3	24.8	18.3	14.2	9.1	5.7	3.8	2.1
	30	---	--	196	110	59.1	25.1	13.4	9.5	6.5	4.4	3.0	1.5
	30^{f}	---	--	•	---	51.1	24.5	12.4	9.2	6.6	4.4	2.9	1.6
0.5	0	7.8	92	277	88	57.9	27.8	23.6	18.0	9.5	5.1	3.1	1.6
	10	5.9	70	249	111	64.4	24.6	17.9	13.1	8.5	5.3	3.6	2.0
	30	---	--	207	101	65.1	26.9	14.9	10.7	7.1	4.6	3.1	1.5
	30^{f}	---	--	•	---	90.0	27.1	13.6	9.5	6.6	4.5	3.0	1.5
1.0	0	7.8	92	280	93	59.1	27.6	23.3	17.9	9.4	5.1	3.2	1.7
	10	5.9	70	236	100	70.1	26.3	18.5	13.1	8.0	4.9	3.1	1.7
	30	---	--	193	112	50.6	26.1	13.6	9.3	6.2	4.2	3.0	1.5
	30^{f}	---	--	•	---	33.5	25.3	13.1	9.2	6.6	4.6	3.1	1.7
5.0	0	7.8	92	276	93	62.4	26.4	22.5	17.6	9.4	5.2	3.2	1.7
	10	6.4	76	256	114	75.5	25.4	18.5	13.2	8.5	5.5	3.7	1.7
	30	---	--	179	121	41.2	23.2	12.0	8.3	5.7	4.0	2.9	1.5
	30^{f}	---	--	•	---	29.6	22.5	10.8	7.5	5.5	4.1	3.0	1.8
10.0	0	7.8	92	270	93	59.0	25.9	22.0	16.9	9.4	5.2	3.2	1.6
	10	6.4	76	246	120	59.5	23.6	16.9	12.5	8.2	5.4	3.7	2.1
	30	---	--	187	128	34.3	22.0	12.0	8.5	6.0	4.3	2.1	1.7
	30^{f}	---	--	•	---	23.5	21.9	12.3	8.9	6.6	4.7	3.2	1.7

•Light capacities were not obtained in these samples due to a computer malfunction.

Footnotes on page 125.

Footnotes to Tables 40-45

a. Stored oxalate components initially contained 0.133 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), and .003 M 9,10-bis(phenylethynyl) anthracene (BPEA) in dibutyl phthalate (DBP).

b. Unless otherwise indicated oxalate component was stored in six-inch polyethylene lightsticks in contact with an N51A glass pod of activator component. Oxalate components were evaluated against a single lot of activator component (1.5 M H_2O_2 and 6.25 x 10^{-4} sodium salicylate in a solvent mixture of 80% dimethyl phthalate, 20% t-butanol).

c. Determined by infrared spectroscopy.

d. Light capacity in lumen hours per liter.

e. Time required for emission of 75% of the total light.

f. These oxalate components were evaluated against activator component which had been stored concurrently for 30 days under the indicated conditions.

g. Percentage of the original amount of H_2O_2 present as determined by iodometric titration.

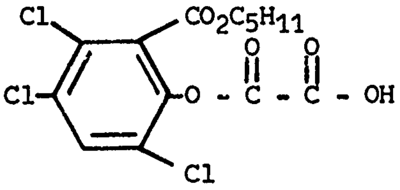
h. PTCS is pentyl 3,5,6-trichlorosalicylate.

i. Data not available.

indicated amount of silica gel, centrifuged and the clear supernatant stored in lightsticks. No induction periods were noted in any of the samples or the control even when the stored activator was used. However, a slight reduction in the early intensities was noted with increasing amounts of silica gel. No significant differences in light capacities were noted after 30 days in the humidity oven.

B. Hydrolysis of CPPO

A possible source of the induction period observed after humidity storage of certain batches of oxalate component is the presence of small amounts of the half-ester of oxalic acid and pentyl 3,5,6-trichlorosalicylate (1).

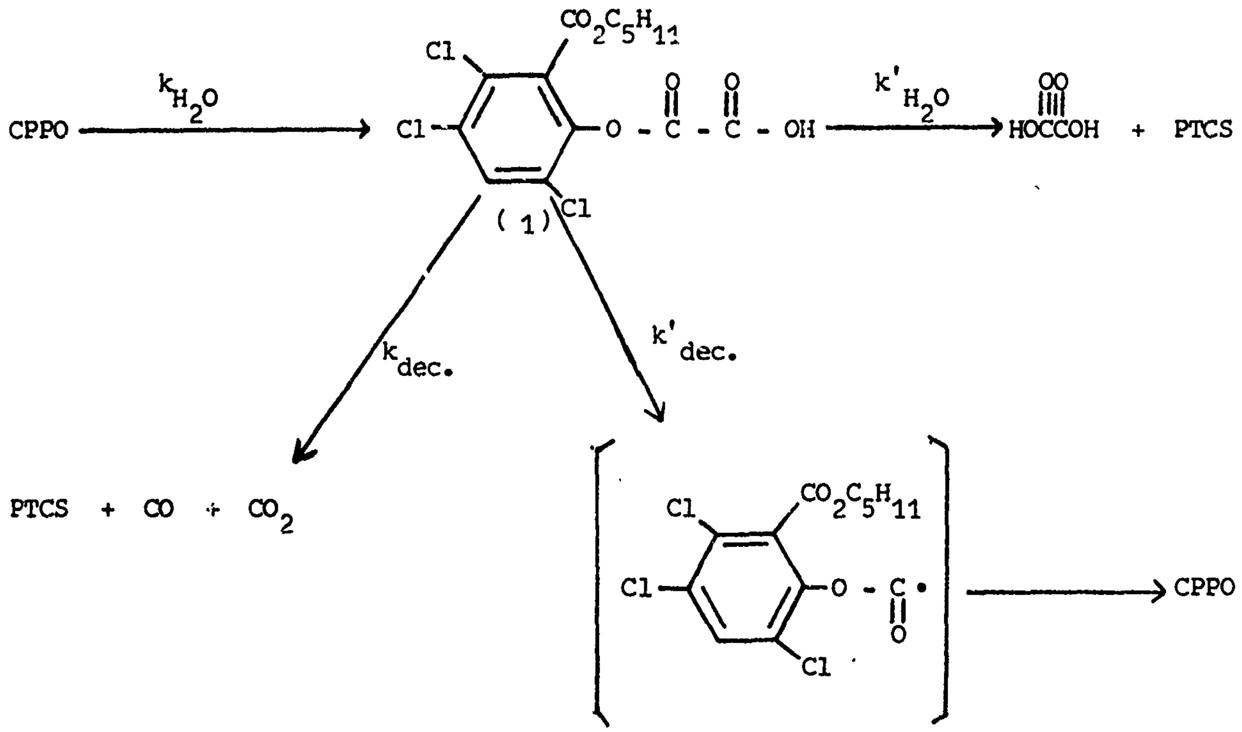


(1)

We have attempted to prepare this acid by slow addition of the potassium salt of pentyl 3,5,6-trichlorosalicylate to a four fold excess of oxalyl chloride, evaporation of the excess oxalyl chloride and hydrolysis of the resulting acid chloride. The diester, CPPO, was isolated from this reaction in 34% yield and a small amount of a liquid acid was isolated in impure form. During the removal of the solvent the temperature exceeded 40°C indicating a thermal decomposition reaction might have taken place. Previously, pentafluoroxalyl chloride was obtained[24] in 60% yield by a similar reaction using only a slight excess of oxalyl chloride. Attempts to prepare <u>1</u> by partial hydrolysis of CPPO were unsuccessful. The results obtained thus far indicate a tentative hydrolysis scheme as outlined in Chart I might be possible.

CHART I

Tentative Scheme for the Hydrolysis of CPPO



The initial step in the hydrolysis probably involves formation of the half-ester (1). This compound can undergo further hydrolysis to oxalic acid or more likely undergo either or both of the decomposition routes indicated. The first pathway could involve formation of PTCS and the gaseous products while the second route might give the intermediate formyl radical which dimerizes to regenerate CPPO. The decomposition of alkyl half-esters of oxalic acid under irradiation has been reported[25] to give yields of diester as high as 78%. This might account for the CPPO formed in the attempted preparation of 1. Since small amounts of oxalic acid completely quench the chemiluminescent reaction it would appear that the half-ester (1) decomposes rather than undergo further hydrolysis ie., $k'_{H_2O} < k_{dec.} + k'_{dec.}$. Heating to rejuvenate an oxalate component having an induction period might involve removing small amounts of 1 by accelerating the decomposition processes. The relatively minor effect of added water on good batches of oxalate component would suggest that k_{H_2O} is relatively small under normal conditions. Moisture analyses have indicated that sufficient water (.20% total) permeates a polyethylene lightstick in 10 days at 100°F, 90% relative humidity to hydrolyze half of the CPPO present. The differences in moisture sensitivity of different samples of oxalate component could be explained by catalytic effects on k_{H_2O}, but further experimental evidence is needed to substantiate this point.

EXPERIMENTAL

Light Measurement

Absolute light measurements were carried out according to the procedures previously described[25] using the spectroradiometer-luminometer developed by Roberts and Hirt.[26] Data was acquired and processed by the methods previously reported.[3]

Physical Measurements

Infrared spectra were obtained with a Perkin-Elmer Model 137 instrument. NMR spectral were recorded on a Varian High Resolution 100 MHZ instrument. Mass spectral measurements were carried out on a Hitachi-Perkin-Elmer Model RMV-6. Absorption spectra were recorded on a Cary Model 14 spectrophotometer. Melting points were measured on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Kinetic Measurements

Fluorescer decomposition rates were measured on a Cary Model 14 spectrophotometer operated with an infrared source and detector in the visible region of the spectrum. In this mode the optics are reversed so that the monochrometer is between the sample and the detector. This allows the long wavelength bands of the fluorescer to be monitored without interference from the chemiluminescent emission. A 15 to 20 ml sample of oxalate component, protected by a drying tube, was stirred magnetically in a water bath at 25.0 ± 1.0°C. After equilibration, the appropriate volume of activator component (1/3 the volume of the oxalate component) was introduced into the flask. At the appropriate time intervals a 0.15 ml aliquot was withdrawn and diluted to 10.0 ml in a volumetric flask. The absorption spectrum was recorded within three minutes after withdrawing the aliquot.

CPPO Analyses

Quantitative analysis for CPPO in oxalate components was carried out on a Beckman IR8 grating instrument. A comparison of the absorbance of the sample in chloroform at 1790 cm^{-1} to the absorbance of a standard oxalate component of known CPPO content was used as the basis of the analytical method.

Formulation of the High Light Capacity System

Preparation of the Standard Activator Component* (1 liter)

Reagent grade sodium salicylate, 0.320g, is weighed into a clean, dry one liter volumetric flask containing a magnetic stirring bar, and 500 ml of 30% (by volume) dimethyl phthalate (Tennessee Eastman) - 20% t-butanol (Shell Chemical Company) is added to the flask. To the stirred mixture, 52.1g of 98% hydrogen peroxide (FMC Corporation) previously weighed into a clean, dry glass beaker is slowly added (Caution! 98% hydrogen peroxide is a strong oxidant. Handle with care. Avoid contamination by not returning unused hydrogen peroxide to the original bottle). Additional 80% dimethyl phthalate 20% t-butanol is added to just below the mark and the solution stirred for two hours at room temperature. The stirrer is removed and additional 80-20 solvent added to the mark and the flask shaken to effect complete solution. The activator is stored in Teflon^R FEP containers.

*For the high intensity activator component 0.640g of sodium salicylate is used. For the long-lived activator component 0.126g of tetramethylammonium 3,5,6-trichlorosalicylate is used.

Preparation of the Oxalate Component

A clean, dry one liter volumetric flask containing a stirring bar is charged with 189.6g of bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO) and 750 ml of dibutyl phthalate (Tennessee Eastman). The flask is then fitted with a calcium chloride drying tube and immersed in an oil bath at 150°C. The flask and contents are stirred for one hour at this temperature. The flask is then removed from the oil bath and allowed to cool to room temperature. At this point 4.406g of 1-chloro-9,10-bis(phenylethynyl)anthracene (1-ClBPEA) and 0.220g of 2,6-di-t-butyl-p-cresol are added, the mixture stirred to effect complete solution and the volume made up to one liter with dibutyl phthalate after removing the stirring bar. The final solution is then stirred magnetically for about 30 minutes.

1-Chloro-9,10-Bis(Phenylethynyl)Anthracene (1-ClBPEA)

The procedure used was a modification of the method of Reid, Donner and

Schlegelmilch.[27] Into a 500 ml round bottom, 3 neck flask fitted with a mechanical stirrer and a reflux condenser protected with a calcium chloride drying tube was charged 200 ml of dioxane (MC and B, scintillation grade) and 32.6g (0.32 mol.) of phenylacetylene followed by 7.36g (0.32 mol.) of lithium amide under a nitrogen atmosphere. While stirring this mixture, 19.2g (0.08 mol.) of 1-chloroanthraquinone was added in several portions. The mixture was refluxed with vigorous stirring for 16 hours and during this period changed from a light orange color to a deep red. Thin layer chromatography showed that only a small amount of unreacted 1-chloroanthraquinone remained. After most of the dioxane was removed on a rotary evaporator under reduced pressure, a solution of 10g of ammonium chloride and 300 ml of water was added to the residue and swirled for 30 minutes. The mixture was allowed to stand for one hour and extracted with several portions of benzene totaling 300 ml. The extract was heated on a steam bath, filtered and the remaining water removed by evaporation of a portion of the benzene on the steam bath. After cooling the benzene extract in ice, petroleum ether was added so that the final volume of solution was one liter. Crude 1-chloro-9,10-bis(phenylethynyl)anthra-9,10-diol precipitated from the solution, was filtered and air dried (30.8g, 86%).

The crude diol (8.58g, 0.019 mol.) was dissolved in 40 ml of dimethyl formamide and 14.7g (0.065 mol.) of stannous chloride dihydrate was added. An exothermic reaction ensured with the immediate precipitation of an

After stirring overnight, the solid was recovered by filtration and washed with methylene chloride. Two recrystallizations (charcoal treated) from benzene afforded 5.69g (72%) of 1-chloro-9,10-bis(phenylethynyl)anthracene, m.p. 203-4 (lit.[28] 205-6); one spot on thin layer chromatography (silica gel); absorption spectrum (in dibutyl phthalate) λ max. 451 nm (ϵ 33,160) and 476 nm (ϵ 36,970).

2-Chloro-9,10-Bis(Phenylethynyl)Anthracene (2-ClBPEA)

The procedure used was a modification of the method of Reid, Donner and Schlegelmilch.[27] Into a 500 ml round bottom flask fitted with a mechanical stirrer a reflux condenser and nitrogen gas inlet was charged successively , 200 ml of dioxane (MC and B, scintillatron grade), 32.6g (0.32 mol.) of lithium amide and 19.4g (0.08 mol.) of 2-chloroanthraquinone. This mixture was refluxed for 16 hours with vigorous stirring under a nitrogen atmosphere. Most of the solvent was removed on a rotary evaporator under reduced pressure and a solution of 10g of ammonium chloride in 300 ml of water was slurried with the residue. The residue was extracted with benzene, the extracts filtered and evaporated partially on a steam bath to remove the residual water. Cooling of the benzene extract and dilution with petroleum ether afforded 23.5g of a very crude product. Recrystallization of this material from benzene-petroleum ether (5:1 by volume) gave 10.8g (30%) of crude 2-chloro-9,10-bis(phenylethynyl)anthra-9,10-diol, m.p. 162-7 (lit.[12] 170-171).

The crude diol (8.58, 0.019 mol.) was added to a solution of 14.70g (0.065 mol.) of stannous chloride in 50 ml of dimethyl formamide. An orange precipitate formed immediately and the reaction was allowed to stand overnight at room temperature. The solid was filtered and washed with dimethyl formamide followed by methylene chloride. Recrystallization from benzene afforded 6.50g (82%) of 2-chloro-9,10-bis(phenylethynyl)anthracene (2-ClBPEA), m.p. 222-5 (lit.[27] 226-7); one spot on thin layer chromatography (silica gel); absorption spectrum (dibutyl phthalate) λ max 442 nm (ϵ 30,720) and 466 nm (ϵ 32,180).

1,4,5,8-Tetrachloro-9,10-Bis(Phenylethynyl)Anthra-9,10-Diol

A slurry of 34.6g (0.1 mole) 1,4,5,8-tetrachloroanthraquinone and 30.6g (0.3 mole) of phenyl acetylene in 500 ml anhydrous dioxane was charged into a one liter creased (Morton) flask. Lithium amide (6.9g, 0.3 mole) was added and the mixture heated to reflux. The initial slurry was yellow and turned brown, then grey as reflux continued. After 96 hours of reflux about 200 ml of solvent was distilled out. The cooled reaction was hydrolyzed with 400 ml of water containing 16.1g of NH_4Cl. A brown tar was separated from the hydrolysis mixture by decanting.

Washing of the tar with hexane afforded a solid. Boiling of this solid with acetone resulted in an off-white solid which was collected by filtration, washed with acetone and dried, yielding 42.6g of crude 1,4,5,8-tetrachloro-9,10-bis-(phenylethynyl)anthra-9,10-diol, m.p. 272-276°C (dec.), 77% yield. Infra-red spectrum is in agreement with the desired product. The crude diol was crystallized from 1400 ml toluene, yielding 25.8g (61%) of purified material, m.p. 284-286°C (dec., softening from 260°C). The analytical sample was prepared by recrystallization from chloroform-hexane.

Calcd. for $C_{30}H_{16}O_2Cl_4$: C, 65.47; H, 2.93; Cl, 25.77.

Found: C, 64.77; H, 2.83; Cl, 26.38.

Several attempts to reduce this diol to 1,4,5,8-tetrachloro-9,10-bis(phenylethynyl) anthracene with stannous chloride under a variety of conditions were unsuccessful due to the formation of large amounts of by-products which could not be separated from the desired product.

1,8-Dichloro-9,10-Bis(Phenylethynyl)Anthra-9,10-Diol

A mixture of 22.4g (0.22 mole) of phenylacetylene and 5.0g (0.22 mole) lithium amide was refluxed two hours in 500 ml of anhydrous dioxane. Solid 1,8-dichloroanthraquinone (27.7g, 0.1 mole) was added in portions to the dioxane solution and the resulting mixture was refluxed for 36 hours. About half of the dioxane was distilled from the reaction mixture and a solution of 12.5g of ammonium chloride in 400 ml of water was added slowly to the cooled reaction. The aqueous phase was decanted off after 15 minutes of stirring, leaving a sticky solid. Washing with 250 ml benzene and filtering gave 36.6g of solid. Evaporation of the benzene filtrate gave an additional 10.0g of crude solid. The combined crude yield was 97%. Recrystallization of the crude diol from 600 ml of toluene afforded 35.1g (73%) of pure 1,8-dichloro-9,10-bis(phenylethynyl)anthra-9,10-diol, m.p. 219-221°C (uncorr.).

1,8-Dichloro-9,10-Bis(Phenylethynyl)Anthracene (1,8-DCBPEA)

A solution of 1,8-dichloro-9,10-bis(phenylethynyl)anthracene-9,10-diol (35.1g, 0.073 mole) and 55g of reagent grade $SnCl_2 \cdot 2H_2O$ in 500 ml of DMF was stirred at room temperature for 96 hours. The red-orange solid present was collected by filtration washed with methylene chloride, and dried under vacuum to obtain 25.6g (78%) of 1,8-dichloro-9,10-bis(phenylethynyl)anthracene, m.p. 165-167 dec. An additional 5.6g of crude 1,8-DCBPEA was obtained from the filtrate of the first crop by the addition of 200 ml of water. The first crop (25.6g) was recrystallized from toluene (ca. 200 ml), yielding 20.4g (62%) of pure 1,8-dichloro-9,10-bis(phenylethynyl)anthracene; TLC (silica gel, 4:1 petroleum ether-benzene), one spot at $R_f = 0.72$; λ max. (benzene) 495 nm ($\epsilon = 31,600$); 471 nm(ϵ 28,200).

2-Phenylethynyl-1,1,1,3,3,3-Hexafluoro-2-Propyl)Oxalate (PEHFO)

Into a dry flask fitted with a magnetic stirrer was charged 5.75g (0.25 mol.) of lithium amide and 30.5g (0.30 mol.) of phenyl acetylene followed by 50 ml of dry dioxane while keeping under a nitrogen atmosphere.[28] The resulting mixture was warmed to initiate the evoluation of ammonia and held at 60 to 80° for about 1.5 hours at which point the ammonia evolution slowed appreciably. An additional 75 ml of dioxane was added and the mixture refluxed for 0.5 hour. The mixture was then cooled to 30°, a dry ice condenser added, and the slow addition of 41.5g (0.25 mol.) gaseous hexafluoroacetone initiated. An immediate exothermic reaction ensured with the temperature increasing to 60°. The cooling and addition rate of hexafluoroacetone were adjusted to maintain the temperature at 30-40°. Towards the end of the addition an additional 100 ml of dioxane was added because the reaction mixture had thickened and stirring became difficult. At the end of the addition (one hour), the reaction mixture was poured into a beaker and acidified with hydrochloric acid (30 ml conc. diluted to 100 ml). The aqueous mixture was extracted several times with ether, the ethereal solution washed three times with water and dried over magnesium sulfate.

The ether was evaporated under reduced pressure yielding 78.7g of a red oil. Distillation (68° at 6 mm) afforded 59.0g of an azeotrope consisting of 7% dioxane and 93% (82% yield) of 2-phenylethynyl-1,1,1,3,3,3-hexafluoro-2-propanol (lit.[29] bp for the pure carbinol 81-2° at 7 mm). The composition of the azeotrope was confirmed by nmr and vpc. Related acetylenic hexafluoropropanols have been reported[29,30,31] to form highly stable azeotropes with ethers. The ir spectrum of the product mixture showed the following characteristic absorption bands: 3200-3400 (broad, OH), 2250 ($C \equiv C$), 1220-1260 (broad, CF_3) and 760, 720, 680 cm^{-1} (aromatic hydrogen). The carbinol-dioxane mixture was used without further purification for the preparation of the oxalate ester.

Bis(2-Phenylethynyl-1,1,1,3,3,3-Hexafluoro-2-Propyl)Oxalate

Triethylamine (6.1 ml) was added to a solution of 23.0g of the dioxane-2-phenylethynyl-1,1,1,3,3,3-hexafluoro-2-propanol mixture (containing 0.08 mol. of carbinol) in 200 ml of anhydrous ether. The resulting solution was cooled in an ice bath and a solution of 3.8 ml (0.45 mol.) of oxalyl chloride in 50 ml of ether was added dropwise with stirring over 40 minutes. The ice bath was removed and the solution allowed to warm to room temperature over one hour. Vpc at this point indicated a mixture of 60% unreacted carbinol and 40% product. Refluxing the mixture for three hours did not change this ratio, so an additional 2.2 ml of oxalyl chloride and 1.0 ml of triethylamine was added and the solution refluxed overnight. Vpc indicated approximately equal proportions of carbinol and product. The mixture was filtered to remove the amine hydrochloride and the ether evaporated to leave an amber oil. Three recrystallizations from 30-60° petroleum ether (charcoal added to decolorize), chilling the solution in dry ice to crystallize the product, afforded 3.4g (14%) of bis(2-phenylethynyl-1,1,1,3,3,3-hexafluoro-2-propyl)oxalate, m.p. 60.5-61.5; ir (Nujol), 2250, 1800, 1240, 760 and 685 cm^{-1}.

Anal. Calcd. for $C_{24}H_{10}F_{12}O_4$: C, 48.83; H, 1.83; F, 38.51.

Found: C, 48.78; H, 1.72; F, 38.04.

Bis(3-Phthalidyl)Oxalate

A solution of 15.0g (0.10 mole) of phthaldehydic acid (Aldrich) in 60 ml of tetrahydrofuran (THF) was clarified by filtration through Hyflo^R filter aid. A solution of 4.2 ml (0.05 mol.) of oxalyl chloride in 10 ml THF was added to the filtrate with no evident reaction. Pyridine (8.1 ml, 0.10 mole) in 40 ml THF was added dropwise to the stirring solution over a two hour period while maintaining the temperature below 30°. A white precipitate formed after approximately a third of the pyridine had been added. The solution was stirred for 0.5 hour after the addition, refluxed four hours, allowed to stand overnight and refluxed an additional two hours. The hot solution was filtered, leaving a white solid, which was washed with petroleum ether (30-60°): yield 23.3g. This solid was then slurried with 100 ml of absolute ethanol, filtered, washed with petroleum ether and air dried, yielding 12.7g of a white solid, m.p. 201-210 dec. Recrystallization from hot (not refluxing) dimethyl formamide, washing with absolute ethanol and petroleum ether afforded 5.1g (36%) of a white solid m.p. 230-232 dec. Further recrystallizations from dimethyl formamide gave the analytical sample of bis(phthalidyl)oxalate m.p. 233-235°.

<u>Anal.</u>	Calcd. for $C_{18}H_{10}O_8$:	C, 61.03;	H, 2.82.
	Found:	C, 61.23, 61.21;	H, 2.90, 2.77.

The ir spectrum (Nujol) was consistent with the bis(3-phthalidyl)oxalate structure: 1780 (oxalate carbonyl), 1760 (lactone carbonyl) and 970 cm^{-1} (symmetric C-O-C stretch characteristic of 3-phthalidyl esters^{20}). An nmr spectrum was obtained after dissolving the oxalate ester in boiling hexamethylphosphoramide: τ 0.62 (broad singlet, relative intensity 0.4, $\overset{\underset{\|}{O}}{C}\underline{H}$), τ 1.75-2.50 (complex multiplet, relative intensity 4.0, Ar-$\underline{H}$) and τ 3.35 (broad singlet, relative intensity 0.5, Ph-C$\underline{H}$ $(\overset{\underset{\|}{O}}{O C}-)_2$. The presence of both aldehyde and methine protons in the spectrum indicated a rearrangement might have taken place under these rather rigorous conditions.

Bis(2-Cyano-1,1,1,3,3,3-Hexafluoropropyl)Oxalate (CNHFO)

A 250 ml, three neck flask fitted with dry ice condenser, stirrer, gas inlet and calcium chloride drying tube was flamed dry under a stream of nitrogen. Sodium cyanide (4.9g, 0.10 mol.) and 100 ml anhydrous tetrahydrofuran (THF) were charged into the flask. Hexafluoroacetone (16.6g, 0.10 mol.) was distilled into the flask and the sodium cyanide slowly dissolved. The solution was refluxed vigorously for two hours after the addition of the hexafluoroacetone. A solution of oxalyl chloride (6.3g, 0.05 mol.) in 50 ml of anhydrous THF was added to the cooled solution over a period of 20 minutes and the mixture was refluxed for two hours. The hot solution was filtered to remove the precipitated sodium chloride, and the solvent removed by evaporation under reduced pressure. Addition of hexane to the oily residue gave crude CNHFO (10.2, 46%), m.p. 109-112°. Recrystallization from benzene afforded 6.1g (28%) of pure CNHFO, m.p. 113-114.5°. IR (Nujol): 2280 (very weak), 1830 (m), 1290 (s), 1240 (s), 1120 (m), 1090 (m), 980 (m) and 720 cm^{-1}. Mass spectrum (70 eV) m/e 421 (M-19), 220 (M/2), 176 (M/2-44); other strong ions at m/e 157, 147, 119, 97 and 69.

<u>Anal.</u>	Calcd. for $C_{10}F_{12}N_2O_4$:	C, 27.29;	N, 6.36.
	Found:	C, 25.99;	N, 6.27.

Bis(2-Nitro-4-Chloro-6-Carbopentoxyphenyl)Oxalate (NCPO)

Into a one liter Morton flask fitted with a mechanical stirrer and thermometer was charged 69.2g (0.40 mol.) of 5-chlorosalicylic acid and 300 ml of water. While stirring, 38.5 ml (0.60 mol. HNO_3) of concentrated nitric acid was added resulting in a slight exotherm (to about 35°). The flask was then immersed in a warm water bath and the heterogeneous mixture stirred vigorously for four hours at 60-70°. The mixture was poured onto ice, filtered and air dried overnight yielding 77.7g of crude product, m.p. 142-150. This solid was dissolved in 2.2 liters of boiling benzene, the solution treated with activated charcoal and concentrated to approximately 1/4 of the original volume. Cooling, filtering and drying afforded 46.6 (53%) of 3-nitro-5-chlorosalicylic acid; m.p. 162-164.5 (lit.[32] m.p. 162-163°; ir (Nujol), 1670, 1520, 1350, 1230, 1180 (doublet), 910, 800, 720 and 700 cm^{-1}; nmr (dimethyl sulfoxide) showed an AB pattern at 1.82 τ and 1.71 τ (J = 3Hz) along with exchangeable protons.

Into a one liter round bottom flask fitted with a reflux condenser, Dean-Stark trap and a magnetic stirrer was charged 43.5g (0.20 mol.) of 3-nitro-5-chlorosalicylic acid, 2.0g of p-toluene sulfonic acid monohydrate, 450 ml of n-pentanol and 300 ml of toluene. This mixture was refluxed for 48 hours at which point TLC indicated only a trace of starting material remained. The reaction mixture was washed with two 100 ml portions of 2.5% sodium bicarbonate solution followed by two 100 ml water washes. The organic phase was separated, dried over magnesium sulfate and the solvents removed under reduced pressure on a rotary evaporation leaving a red oil. This oil was dissolved in petroleum ether, treated with charcoal, and the solution chilled in a ice bath. A faintly yellow solid, pentyl 3-nitro-5-chlorosalicylate, was recovered in two crops, m.p. 46-47.5°, yield 37.0g (64%); ir (Nujol), 1680, 1540, 1250, 800 and 730 cm^{-1}.

The pentyl 3-nitro-5-chlorosalicylate (17.3g, 0.06 mol.) was dissolved in 300 ml of benzene and 8.33 ml (6.07g, 0.06 mol.) of triethylamine added. To the stirring solution was added dropwise a solution of 2.81 cc (4.19g, 0.033 mol.) of oxalyl chloride in 60 ml benzene over 20 minutes. After stirring 90 minutes at room temperature, the mixture was refluxed for four hours and allowed to cool overnight. The benzene solution was filtered to remove the triethylamine hydrochloride and the benzene removed on a rotary evaporator under reduced pressure leaving a yellow oil which solidified on addition of hexane and chilling. Filtration afforded a faintly yellow solid in two crops, m.p. 83-5°. Recrystallization from hexane yielded pure NCPO, m.p. 85.5-87; ir (Nujol), 3050, 1680, 1620, 1540, 1350, 1240, 1210 and 1110 cm^{-1}.

Anal. Calcd. for $C_{26}H_{26}Cl_2N_2O_{12}$: C, 49.61; H, 4.16; N, 4.45; Cl, 11.26.

Found: C, 49.68; H, 4.37; N, 4.39; Cl, 11.31.

Found: 49.68; H, 4.37; N, 4.39; Cl,

APPENDIX

Kinetic Data for Fluorescer Decomposition (Figures 17-22)

Unless indicated otherwise chemiluminescent reactions contained 0.375 M H_2O_2, 1.56 x 10^{-4} M sodium salicylate (NaSal) and indicated concentrations of fluorescer and CPPO. The slopes in Figures 17-22 represent the least squares fit of the experimental data. The quadratic effect is a measure of the requirement of a quadratic term to fit the data at the indicated confidence level.

Figure 18

DECOMPOSITION OF 1,8-DCBPEA
CONCENTRATIONS: 3.4 x 10^{-3} M 1,8-DCBPEA, 0.21 M CPPO

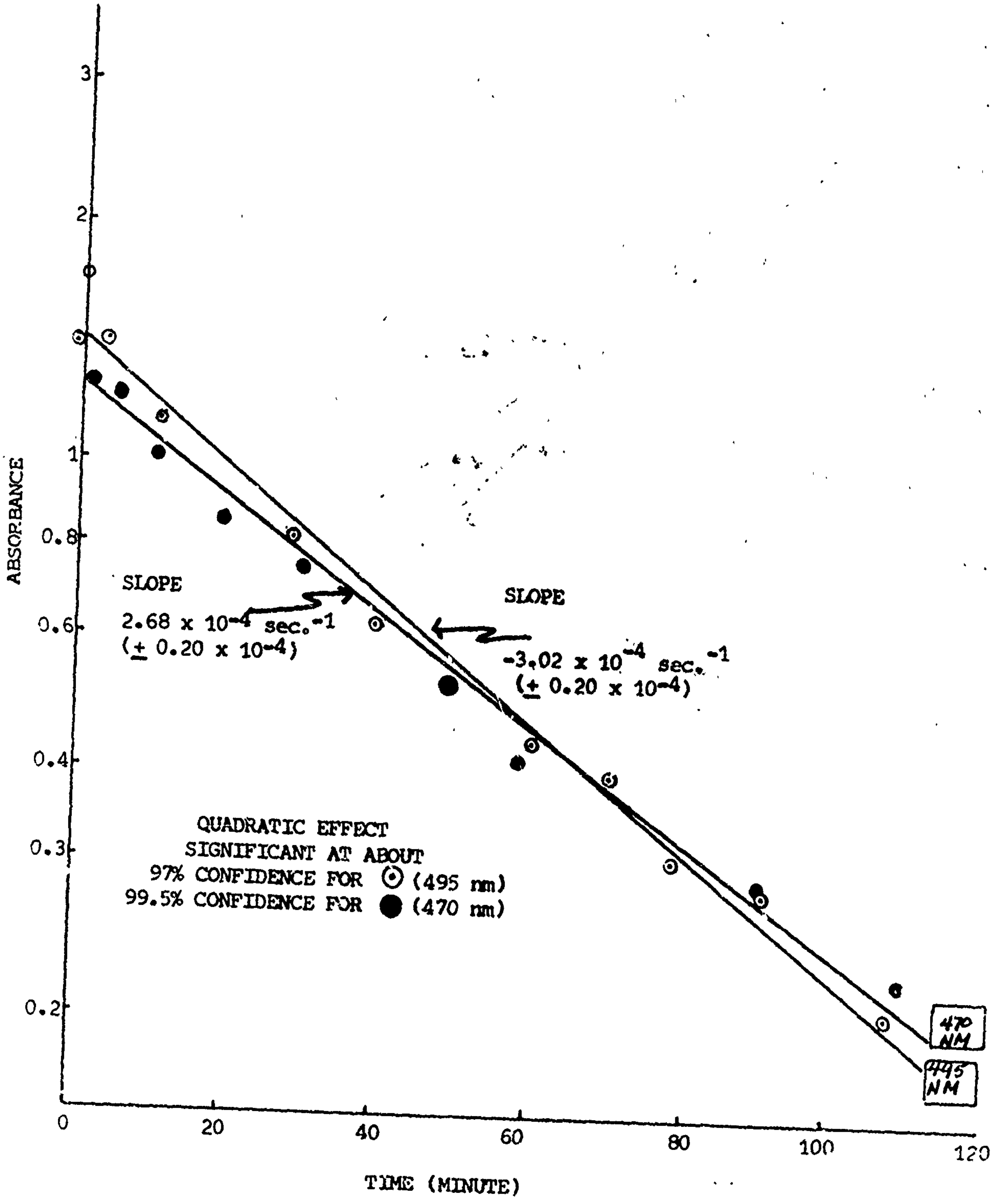


Figure 19

DECOMPOSITION OF 1,5-DCBPEA
CONCENTRATIONS: 1.35×10^{-3} M 1,5-DCBPEA
0.21 M CPPO

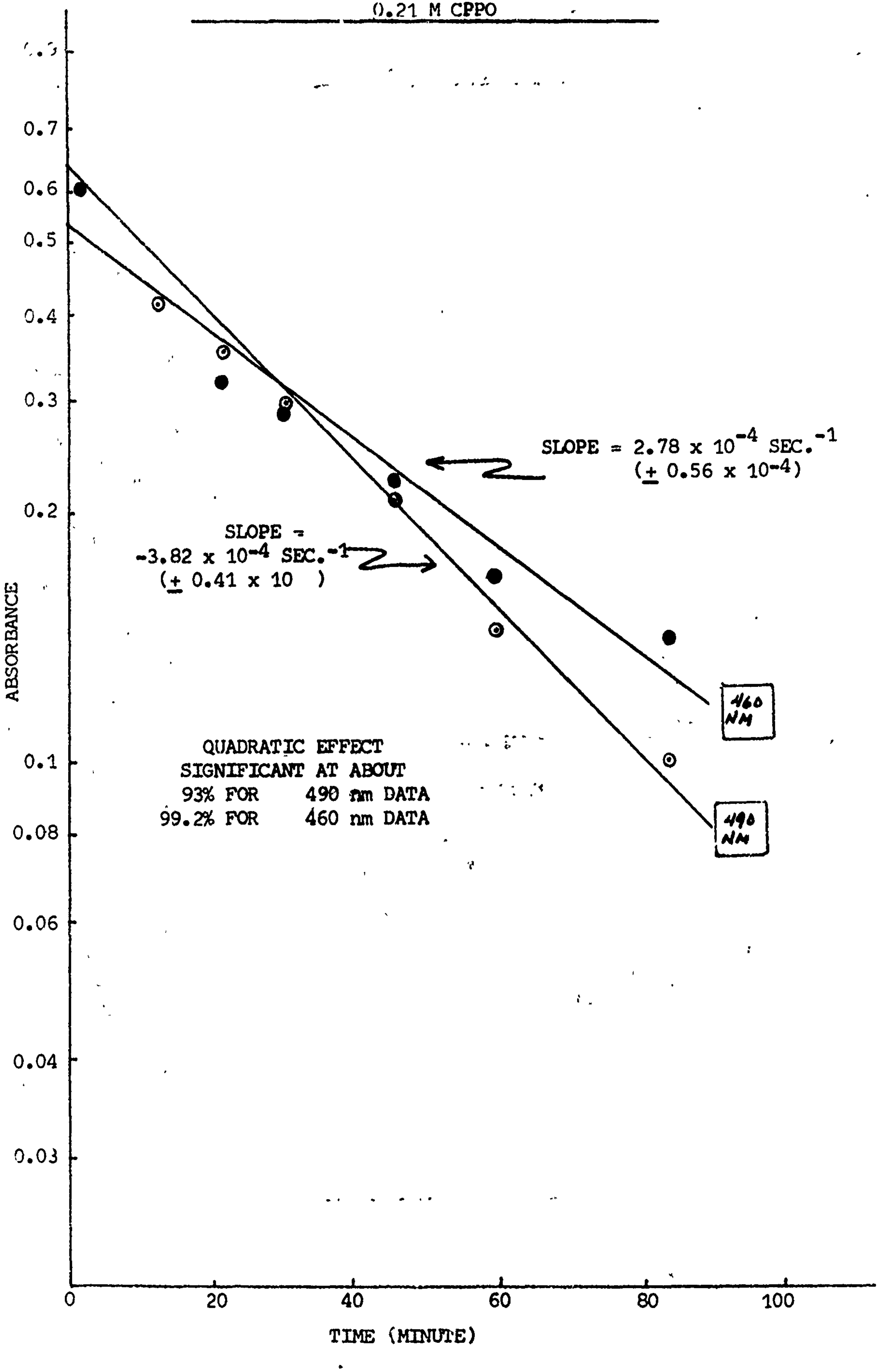
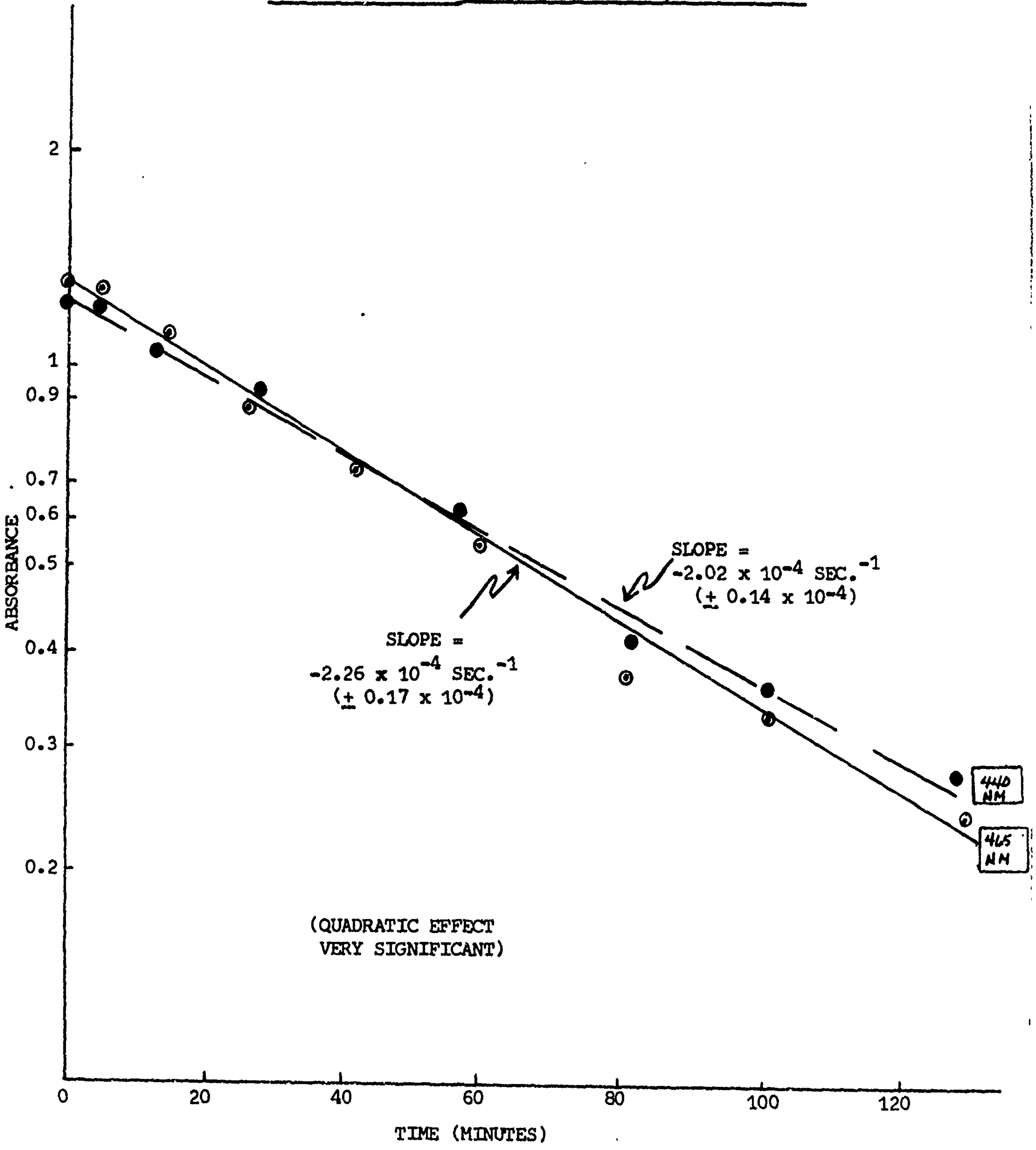


Figure 20

DECOMPOSITION OF BPEA
CONCENTRATIONS: 2.25 x 10^{-3} M BPEA, 0.21 M CPPO



SLOPE = -2.02×10^{-4} SEC.$^{-1}$ ($\pm$ 0.14 x 10^{-4})

SLOPE = -2.26×10^{-4} SEC.$^{-1}$ ($\pm$ 0.17 x 10^{-4})

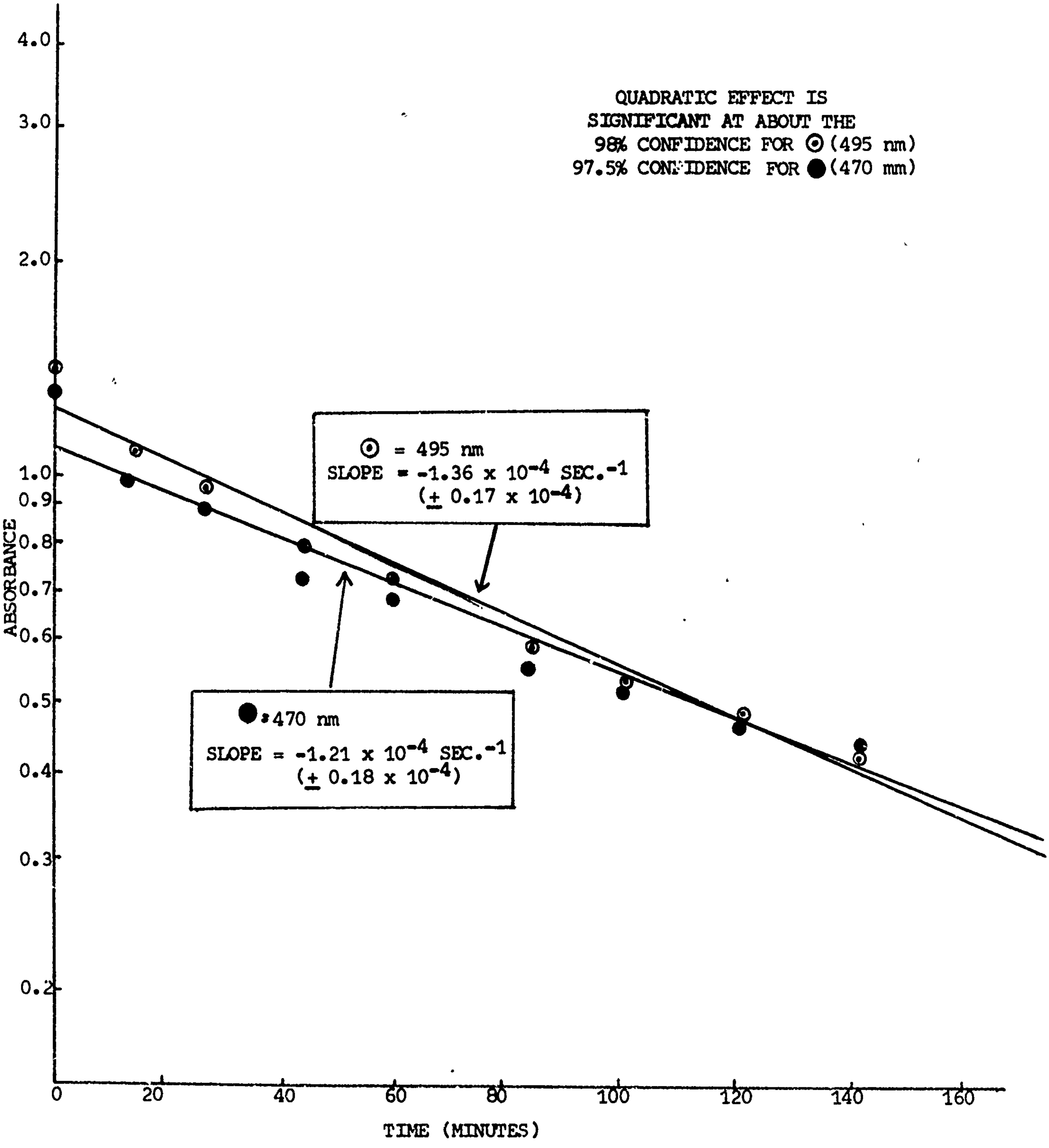
(QUADRATIC EFFECT VERY SIGNIFICANT)

Figure 21

DECOMPOSITION OF 1,8-DCBPEA

CONCENTRATIONS: 3.4 x 10^{-3} M 1,8-DCBPEA, 0.21 M CPPO

0.3% POLYOX WSRN-80



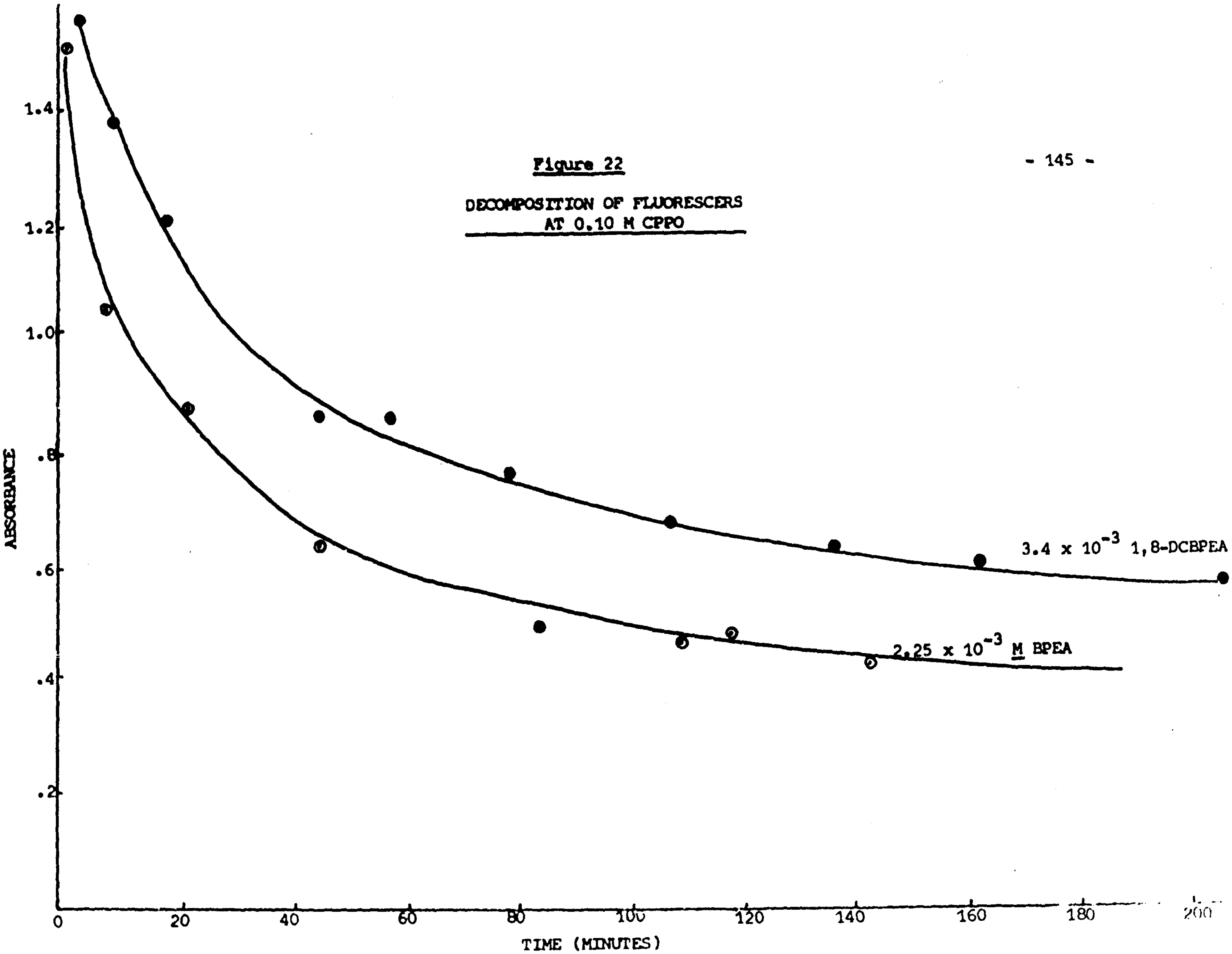
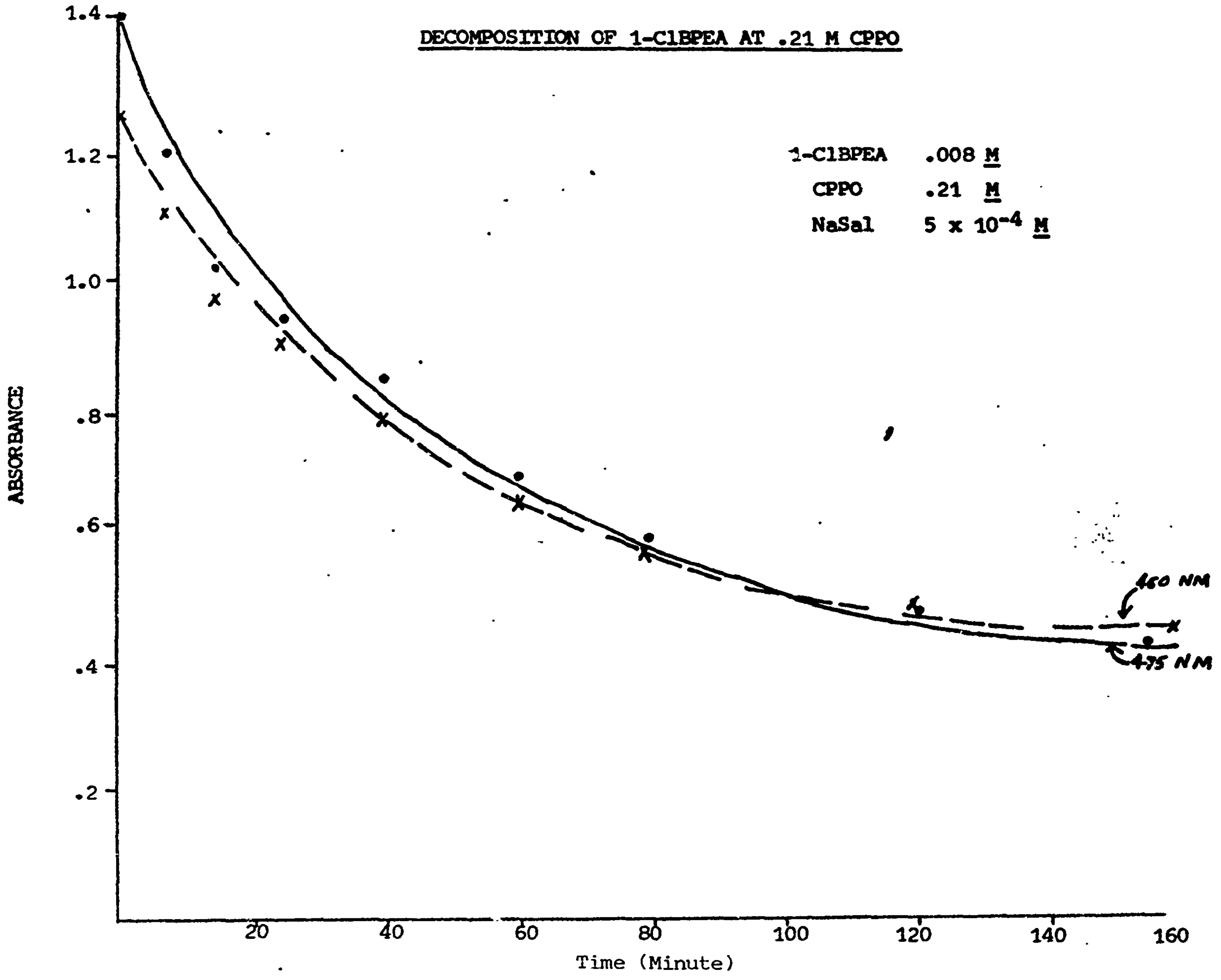


Figure 22

DECOMPOSITION OF FLUORESCERS AT 0.10 M CPPO

FIGURE 23



DECOMPOSITION OF 1-ClBPEA AT .21 M CPPO

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