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LOW INTENSITY, LONG DURATION CHEMILUMINESCENT SYSTEMS. PART 2. --ETC(U)
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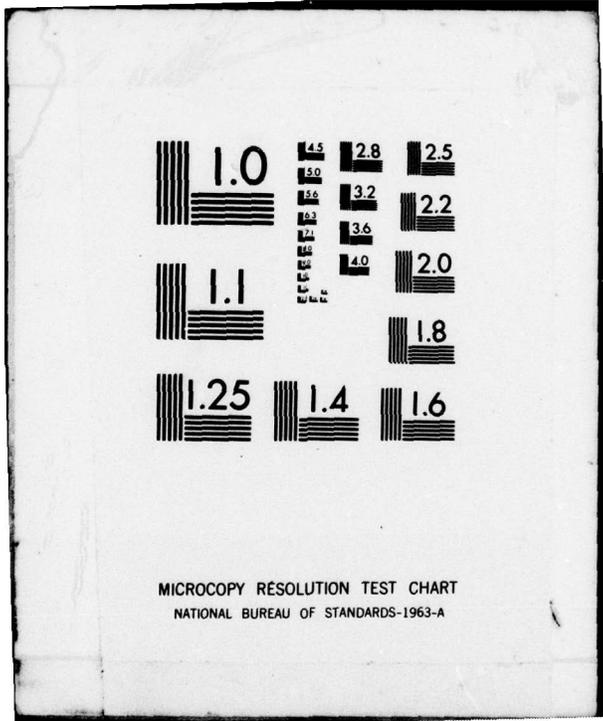
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REPORT

MRL-R-737

LOW INTENSITY, LONG DURATION CHEMILUMINESCENT SYSTEMS

PART 2

CHEMILUMINESCENCE FROM BIS(2,4-DICHLORO-6-CARBOALKOXYPHENYL)OXALATES

Christopher D. Dowd and D. Brenton Paul

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REPORT

14 MRL-R-737-PT-2

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10 Christopher D. Dowd and D. Brenton Paul

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ABSTRACT

Various oxalate esters have been synthesised and their chemiluminescent emission examined in an attempt to produce an improved low intensity, disposable lighting device suitable for 10 hours operation. Derivatives of the bis(2-carboalkoxy-4,6-dinitrophenyl)oxalate series were shown to possess unsuitable stability while the chemiluminescence of the bis(6-carboalkoxy-2,4,5-trichlorophenyl)oxalates was too intense to modify suitably. A number of bis(6-carboalkoxy-2,4-dichlorophenyl)oxalates were prepared and by treatment with various combinations of catalyst and inhibitor satisfactory low intensity light emission could be achieved after a 5 minute induction period. Optimum conditions were: oxalate ester, $2 \times 10^{-2}M$; H_2O_2 , $2 \times 10^{-2}M$; potassium salicylate, $5 \times 10^{-4}M$; oxalic acid, $10^{-4}M$. The storage stabilities and solubilities of the dichloro series of oxalates were superior to those of 2,4,6-TCPO.

Aspects of the synthesis of the substituted salicylic acid precursors to the oxalates are discussed.

The merits of chemiluminescent systems relative to beta lights are considered for the particular case of low level illumination.

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DOCUMENT CONTROL DATA SHEET

Security classification of this page:		UNCLASSIFIED	
1. DOCUMENT NUMBERS:		2. SECURITY CLASSIFICATION:	
a. AR Number:	AR-001-368	a. Complete document:	UNCLASSIFIED
b. Series & Number:	REPORT MRL-R-737	b. Title in isolation:	UNCLASSIFIED
c. Report Number:	MRL-R-737	c. Abstract in isolation:	UNCLASSIFIED
3. TITLE: LOW INTENSITY, LONG DURATION CHEMILUMINESCENT SYSTEMS PART 2 CHEMILUMINESCENCE FROM BIS(2,4-DICHLORO-6-CARBOALKOXYPHENYL)OXALATES			
4. PERSONAL AUTHOR(S):		5. DOCUMENT DATE:	
DOWD, Christopher D. and PAUL, D. Brenton		JANUARY, 1979	
6. TYPE OF REPORT & PERIOD COVERED:			
7. CORPORATE AUTHOR(S):		8. REFERENCE NUMBERS:	
Materials Research Laboratories		a. Task: (RD/P7) RD71-72/Q	
		b. Sponsoring Agency: AHQ RR 1092/73	
9. COST CODE:			
10. IMPRINT (Publishing establishment)		11. COMPUTER PROGRAMME(S):	
Materials Research Laboratories, P.O. Box 50, Ascot Vale, Vic.3032		(Title(s) and language(s)):	
JANUARY, 1979			
12. RELEASE LIMITATIONS (of the document):			

Approved for Public Release

12-0. OVERSEAS:	N.O.	P.R.	1	A	B	C	D	E
13. ANNOUNCEMENT LIMITATIONS (of the information on this page):								
No Limitation								
14. DESCRIPTORS:								
Chemiluminescence; Low light level viewing; Oxalates; Oxidation; Additives; Catalysts; Retardants; Chemical reactions; Stability.								
15. COSATI CODES: 0704								

16. ABSTRACT (if this is security classified, the announcement of this report will be similarly classified):

Various oxalate esters have been synthesised and their chemiluminescent emission examined in an attempt to produce an improved low intensity, disposable lighting device suitable for 10 hours operation. Derivatives of the bis(2-carboalkoxy-4,6-dinitrophenyl)oxalate series were shown to possess unsuitable stability while the chemiluminescence of the bis(6-carboalkoxy-2,4,5-trichlorophenyl)oxalates was too intense to modify suitably. A number of bis(6-carboalkoxy-2,4-dichlorophenyl)oxalates were prepared and by treatment with various combinations of catalyst and inhibitor satisfactory low intensity light emission could be achieved after a 5 minute induction period. Optimum conditions were: oxalate ester, $2 \times 10^{-2}M$; H_2O_2 , $2 \times 10^{-2}M$; potassium salicylate, $5 \times 10^{-4}M$; oxalic acid, $10^{-4}M$. The storage stabilities and solubilities of the dichloro series of oxalates were superior to those of 2,4,6-TCPO.

Aspects of the synthesis of the substituted salicylic acid precursors to the oxalates are discussed.

The merits of chemiluminescent systems relative to beta lights are considered for the particular case of low level illumination.

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LOW INTENSITY, LONG DURATION CHEMILUMINESCENT SYSTEMS

PART 2

CHEMILUMINESCENCE FROM BIS(2,4-DICHLORO-6-CARBOALKOXYPHENYL)OXALATES

1. INTRODUCTION

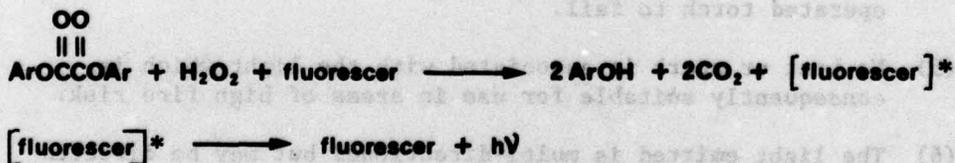
For many night operations under combat conditions the Services require illumination of an intensity such that the task may be performed satisfactorily without disclosing the position of the operators. Tasks in this category would include map and message reading, route and obstacle marking and scale setting. Methods of illumination which must be considered for these purposes are chemiluminescent lighting, the battery operated torch and the beta light. In particular, systems based on chemiluminescence (CL) have several attractive features and these are listed below.

- (1) They are inexpensive and may be considered as disposable items.
- (2) They are light in weight and small in size and therefore easily carried. The lightsticks may also be activated readily.
- (3) They are non-toxic.
- (4) They are relatively robust and should not be affected adversely in tropical conditions. Once triggered, the light emitted is not affected by harsh treatment or wet conditions which could, for example, cause a battery-operated torch to fail.
- (5) No heat or spark is associated with the light which is consequently suitable for use in areas of high fire risk.
- (6) The light emitted is multi-directional but may be directed readily with reflectors.
- (7) They may be produced in a range of colours.

These unique characteristics must be compared with those of the battery-operated torch and the beta light. The ordinary torch is relatively heavy and bulky and fails in wet conditions. Batteries can fail without warning, contacts can corrode and cause failure and in particular the globe is subject to damage by accident, carelessness or rough handling. The storage life and the subsequent reliability in service of batteries in tropical environments has always been a problem. Beta lights are useful for operations requiring a low intensity light source. They are produced in a limited colour range and are relatively expensive but have a service life of 10-20 years and have been marketed in a variety of shapes to indicate direction. Both CL systems, when activated, and beta lights are continuous light emitters and require a cover to mask their emission when not in operational use. The induction time and to a lesser degree the storage stability of the CL system appear to be the most important limitations to their use in a low intensity role. Their main challenge to the beta light lies in the more extensive colour range which is available, the possibility of infrared emitters and the fact that they are inexpensive and may be employed as disposable items. For medium to high intensity marking and illumination applications, however, CL systems are clearly more appropriate than beta lights which are only weak light emitters.

It is evident, therefore, that CL has potential to be adapted to many defence applications. In consequence, consideration was given to the possibility of developing a viable CL system for tasks requiring low level illumination.

Since CL emission cannot be arrested once the chemical reaction has commenced, it is desirable that the light capacity of such a system is sufficient to enable operation for the duration of a full night (10 h). The most efficient CL process known is the oxidation of diaryl oxalates by hydrogen peroxide in the presence of a fluorescent compound (Scheme 1) and is used in the only commercially available chemiluminescent lighting device [1-4]. In this system the fluorescer may be selected to enable the optimum compromise between emission wavelength, chemical stability and quantum yield. The high quantum yield of peroxyoxalate CL makes it an attractive candidate for an all-night CL lighting system. Devices similar to the commercial lightstick may be readily produced and, as they are simply activated, light in weight, reasonably robust and easily carried, they possess many of the features required by disposable low intensity lighting units.



SCHEME 1

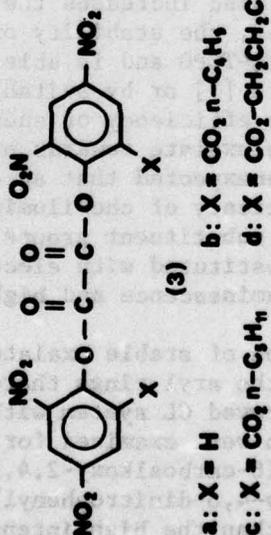
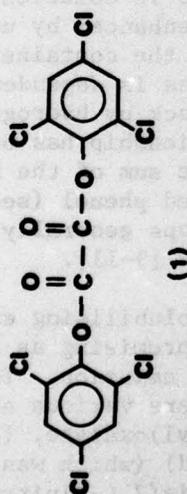
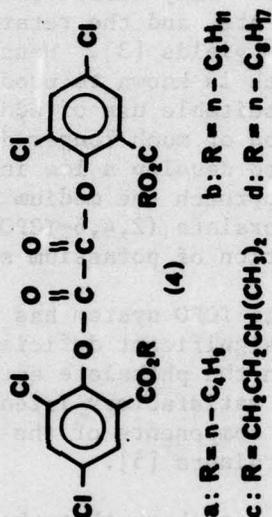
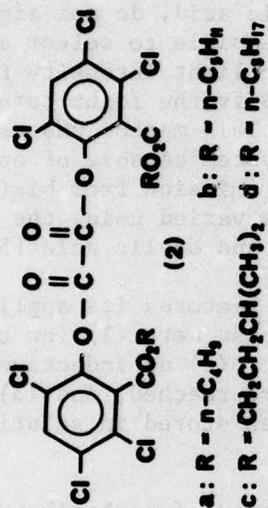
The intensity and duration of the chemiluminescent light output is primarily dependent on the substitution in the aryl rings of the oxalate ester. Modifications to the emission intensity are also possible by changes to the stoichiometry of the system and by introduction of additives which either catalyse or retard the reaction [1-4]. For the purposes of all-night illumination the emission intensity should remain substantially constant over a 10 h period. Individual oxalate esters, however, typically produce an initial burst of light which is followed by a relatively constant but lower intensity output and subsequently by a gradual decline to non-observable levels. Many additives such as the weakly basic catalyst, potassium salicylate, and the retarder, oxalic acid, do not significantly alter the quantum yields [3]. Hence it is feasible to select an oxalate ester system which is known to produce a high light intensity for a short duration and by suitable use of additives modify the light output to a low intensity emission of much longer duration. This method was used in an earlier attempt to develop a low intensity system capable of operating for 10 h. In this approach the medium intensity emission from bis(2,4,6-trichlorophenyl)oxalate (2,4,6-TCPO; (1)) was varied using the buffered additive combination of potassium salicylate and oxalic acid [5].

Although the TCPO system has desirable features its application was limited by some significant deficiencies. These were (1) low solubility of the oxalate in the phthalate ester solvent, (2) an induction time of 5 minutes before satisfactory intensities were reached, and (3) limited stability of the components of the system when stored in solution in polyethylene containers [5].

Experience has shown that the introduction of carboalkoxy groups into the aryl rings not only increases the solubility of the oxalates in phthalate ester solvents but, in the case of bis(6-carbobutoxy-2,4,5-trichlorophenyl)-oxalate (TCCPO; (2a)) and bis(6-carbopentoxo-2,4,5-trichlorophenyl)oxalate (CPPO; (2b)), it also increases the light capacity of chemiluminescence [4,6,7]. Moreover, the stability of these oxalates in solution is greater than that of 2,4,6-TCPO and is able to be further enhanced by use of radical scavengers [7] or by suitable treatment of the container materials [8]. The quantum efficiency of substituted oxalates is dependent on the reactivity of the oxalate towards nucleophilic attack by hydrogen peroxide. Hence it is not unexpected that an empirical relationship has been found between the efficiency of chemiluminescence and the sum of the Hammett sigma constants of the substituent groups on the displaced phenol (see Scheme 1); aryl oxalates substituted with electronegative groups generally produce high intensity chemiluminescence and high quantum yields [9-11].

Modification of stable oxalates possessing solubilising ester substituents on the aryl rings therefore appeared promising as a means for obtaining an improved CL system with long duration emission. Three groups of oxalates which were examined for this purpose were various alkyl derivatives of (a) bis(6-carboalkoxy-2,4,5-trichlorophenyl)oxalate, (2), (b) bis(2-carboalkoxy-4,6-dinitrophenyl)oxalate, (3b-3d) (which was expected to be more soluble than the high intensity material bis(2,4-dinitrophenyl)-oxalate (3a)), and (c) bis(2,4-dichloro-6-carboalkoxyphenyl)oxalate (4). The last mentioned oxalates seemed particularly promising candidates for low intensity, long duration light sources since a consideration of the substituent sigma constants indicated that the emission intensities of these

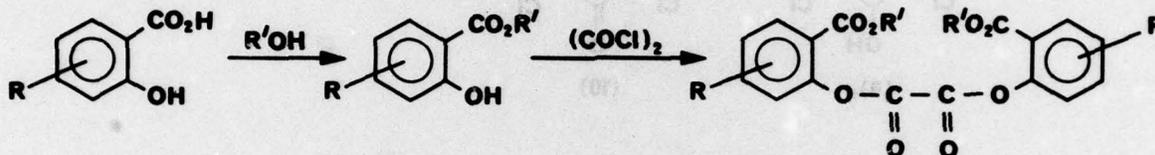
oxalates would be lower than for the trichloro series and therefore more readily modified to the required levels. In addition, the dichloro acids required for their synthesis are intermediates in the synthesis of TCCPO and CPPO. Preliminary results of some aspects of this study have been presented in an earlier report [12].



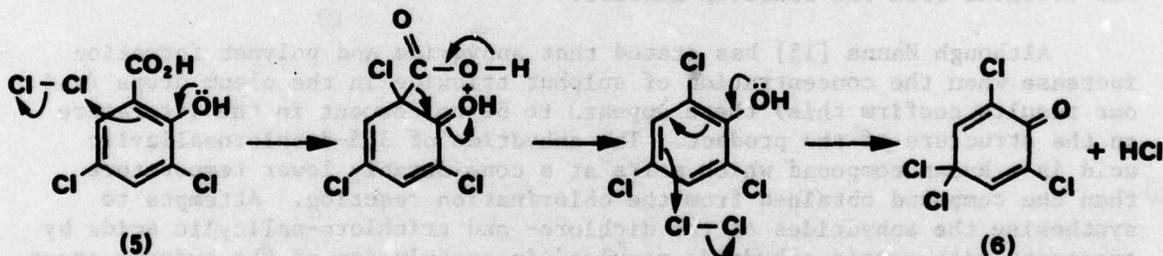
2. RESULTS AND DISCUSSION

2.1 Synthesis of Chemiluminescent Oxalate Esters

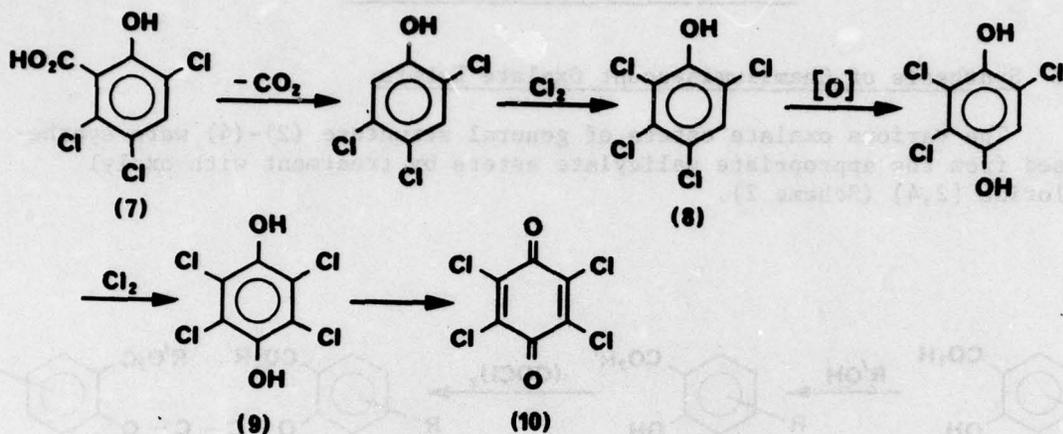
The various oxalate esters of general structure (2)-(4) were synthesized from the appropriate salicylate esters by treatment with oxalyl chloride [2,4] (Scheme 2).



The chlorosalicylic acids were obtained by direct chlorination of salicylic acid and its chloro derivatives. It was found that prolonged chlorination should be avoided since this leads to the formation of byproducts. In the synthesis of 3,5-dichlorosalicylic acid (5), continued chlorination produces 2,4,6,6-tetrachloro-1,4-cyclohexadien-3-one (6). A structural assignment for this material was proposed on the basis of spectra and microanalysis and was confirmed by preparation of an authentic sample. A possible mechanistic route leading to the formation of (6) is shown in Scheme 3.



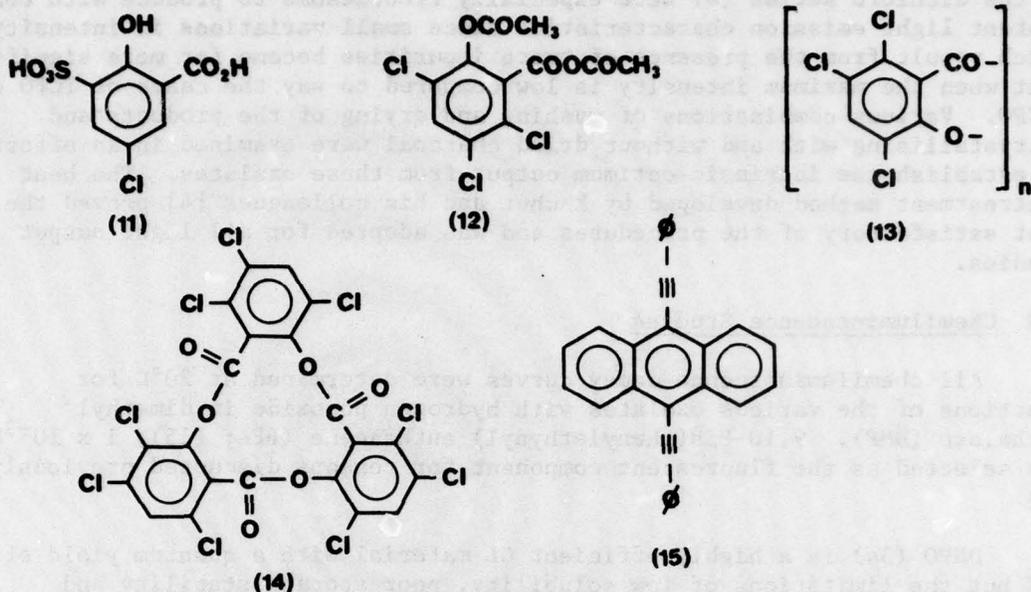
Excessive chlorination of 3,5,6-trichlorosalicylic acid (7) affords two other materials, chloranil (10) and a condensation product (14). It is considered that chloranil is also formed as a result of a prior decarboxylation reaction of the acid as shown in Scheme 4.



SCHEME 4

Support for this proposal is afforded by the observation that 2,3,4,6-tetrachlorophenol (8) is formed when the trichloro acid (7) is chlorinated in 30% acetic acid for several hours [13]. Further, Barral [14] has shown that chloranil is obtained by passing chlorine through a solution of (8) in sulphuric acid at 100° . The logical precursor to chloranil is 2,3,5,6-tetrachlorohydroquinol (9). This compound was also isolated in small yield from reactions which produced chloranil. The chlorinations in oleum are considered to involve an electrophilic substitution with the introduction of a sulphonic acid substituent which is subsequently replaced by a chloro group. Evidence for such intermediates was obtained from the chlorination of a mixture of 5-chloro- and 3,5-dichloro salicylic acid which was terminated before reaction was complete. In this case the sulphonic acid (11) was isolated from the reaction mixture.

Although Hanna [15] has stated that anhydride and polymer formation increase when the concentration of sulphur trioxide in the oleum drops (and our results confirm this) there appears to be no comment in the literature on the structure of the product. The anhydride of 3,5-dichlorosalicylic acid is a known compound which melts at a considerably lower temperature than the compound obtained from the chlorination reaction. Attempts to synthesise the anhydrides of the dichloro- and trichloro-salicylic acids by treatment with acetic anhydride resulted in acetylation of the hydroxy group. With the trichloro acid the reaction was shown to proceed further to give the acetyl derivative of the mixed anhydride of 3,5,6-trichlorosalicylic acid and acetic acid whereas Farinholt and coworkers [15] isolated acetyl 3,5,6-trichlorosalicylic acid by an essentially similar method.



The chlorination product showed a carbonyl band at 1780 cm^{-1} which indicates that the anhydride moiety is not present. In addition there is no hydroxyl peak in the infrared spectrum and an attempted acetylation with acetic anhydride was unsuccessful. The material analyses for $(\text{C}_7\text{HO}_2\text{Cl}_3)_n$ and from previous studies in the salicylic acid [16] and dichlorosalicylic acid [17] series is considered to be a trichlorosalicylide of general structure (13). The molecular weight of the compound, obtained by vapour pressure osmometry, indicates each molecule contains three salicylide units. The cyclic structure (14) which is consistent with the above data is therefore assigned to this product. It is of interest to compare this result with that for the salicylide from dichlorosalicylic acid which was shown to contain four units to the molecule [17].

A preliminary attempt to esterify the trichloro acid (7) by heating under reflux with butanol and sulphuric acid catalyst was unsuccessful. As this method proceeds satisfactorily with salicylic acid the steric crowding in the trichloro acid must prevent esterification. Two other approaches which were examined were (a) incorporation of a Dean-Stark trap in the original reaction procedure and (b) use of the Vilsmeier-Haack reagent, SOCl_2 -DMF, to generate the acid chloride followed by reaction with the appropriate alcohol. Although the second process was successful, the salicylide (14), was also produced. As the esterification with the water trap was a cleaner procedure and afforded satisfactory yields it was used for the synthesis of the entire series of esters.

The oxalate esters were synthesised by the standard method [2,4] and only minor modification to the workup procedure was necessary for individual compounds. Adherence to strictly anhydrous conditions during all synthetic operations was essential in order to obtain reproducible light characteristics from each compound. In particular it was necessary to purify the

phenolic materials thoroughly before conversion to the oxalate. The oxalates of the dichloro series (4) were especially troublesome to produce with consistent light emission characteristics since small variations in intensity which result from the presence of trace impurities become far more significant when the maximum intensity is low compared to say the cases of TCPO or TCCPO. Various combinations of washing and drying of the products and recrystallising with and without dried charcoal were examined in an effort to establish the intrinsic optimum output from these oxalates. The heat pretreatment method developed by Rauhut and his colleagues [4] proved the most satisfactory of the procedures and was adopted for all light output studies.

2.2 Chemiluminescence Studies

All chemiluminescence decay curves were determined at 20°C for reactions of the various oxalates with hydrogen peroxide in dimethyl phthalate (DMP). 9,10-Bis(phenylethynyl) anthracene (BPA; (15); $1 \times 10^{-3}M$) was selected as the fluorescent component for reasons discussed previously [5].

DNPO (3a) is a highly efficient CL material with a quantum yield of 23% but the limitations of low solubility, poor storage stability and unacceptably large concentration quenching have prohibited its use in practical lighting systems [1,2,18]. As expected, the dinitrocarboalkoxy-oxalates (3b-3d) possess improved solubility, relative to DNPO, in phthalate ester solvents and concentrations of 0.1M can be achieved (cf. 0.02M for DNPO). The initial intensities obtained from these oxalates, however, were not greatly superior to those achieved with DNPO or 2,4,6-TCPO (1) and were considerably inferior to those produced by oxalates of the trichloro-carboalkoxy series (4). It was also apparent that, compared with DNPO, the emission from oxalates such as (3b-3d) was much longer lived. These observations confirm the findings made by Rauhut and his coworkers on the CL of bis(2,4-dinitro-6-carbobutoxyphenyl)oxalate (3b) of which we became aware during the course of this study. Differences in light emission between the n-butyl (3b), n-pentyl (3c), and 3'-methylbutyl (isoamyl; 3d) members of the series were negligible and the decay curve (Fig. 1) is characteristic of all three oxalates. All were most unstable and deteriorated rapidly on storage. Decomposition took place when the oxalates were heated in an oven above 60° and, even after standing in a charged, evacuated desiccator for 48 h, sufficient hydrolysis occurred to alter the light emission curves substantially. These oxalates were clearly impractical as an energy source for a low intensity lighting system and investigation of this series was therefore terminated.

Four oxalates of the 2,4-dichloro-6-carboalkoxy series (4) were synthesised. Of these the n-pentyl (4b) and n-octyl (4d) derivatives were obtained as liquids and all attempts to purify the two compounds produced sufficient decomposition or hydrolysis to attenuate their CL intensity. The variation in light emission from the solid oxalates (4a) and (4c), however, was so minimal that extensive examination of only the isoamyl derivative (DCCAPO; 4c) was carried out. This material was selected because it was more readily purified and possessed better storage stability than the butyl ester.

The effects of various concentrations of catalyst (potassium salicylate) and inhibitor (oxalic acid) on the light emission produced from DCCAPO were examined in a similar manner to the study [5] involving 2,4,6-TCPO and 2,4,5-TCPO. In that investigation it was shown that for low level illumination purposes the most suitable intensity range was 8 to 40 units (see Experimental Section). It was considered desirable to narrow these limits, if possible, to between 10 and 30 units.

Previous experience indicated that the oxalate concentrations required to produce this level of intensity over a 10 hour period could be assessed from the light emission curves produced without additives. In Fig. 2 the variation in CL intensity with time is shown for oxalate concentrations from $10^{-2}M$ to $5 \times 10^{-2}M$ using equimolar concentrations of hydrogen peroxide. The series of maxima noted with 2,4,6- and 2,4,5-TCPO also occur with the oxalates (4) and are considered to result from several reaction pathways which all lead to the key dioxetan intermediate but which proceed at different rates [5]. Fluctuations in temperature could have a marginal effect but these are discounted since the curves are reproducible. The light emission characteristics of these oxalates in fact closely approach the required levels. A deficiency of the systems without additives, however, is the induction time of 15 to 20 minutes before useful intensities are achieved. Moreover a system buffered by additives is less susceptible to hydrolysis and has better long term storage performance. It is apparent from Fig. 2 that an oxalate concentration of greater than $10^{-2}M$ is necessary to achieve an adequate intensity over an extended period. A concentration of $2.5 \times 10^{-2}M$ was selected for most of the additional experiments. The effect of increasing the ratio of hydrogen peroxide to oxalate was examined but this had less influence on CL intensity than for the TCPO and DNPO cases [5,18]. A typical curve for 0.05M H_2O_2 and 0.025M oxalate is shown in Fig. 2.

The effects of potassium salicylate and of oxalic acid on CL intensity (Figs 3-5) are virtually insignificant when used in concentrations of $10^{-5}M$ or less (e.g. see Fig. 5). At concentrations of $10^{-3}M$ both additives produce a dramatic change in the light emission curves. For potassium salicylate this is shown in Fig. 4 and although the data for $10^{-3}M$ oxalic acid were not included in Fig. 5 the trend is evident from the decay curves obtained with $10^{-4}M$ and $10^{-5}M$ additives. The relative magnitude of the effects of catalyst and inhibitor appear to be approximately equivalent and when used in equimolar concentrations they tend to counterbalance (Fig. 6). The overall effect relative to the case without additives (Fig. 1) is a slight decrease in maximum intensity and an increase in elapsed time before the minimum desired intensity of 8 units is achieved. This suggests that the oxalic acid is marginally more dominant than the potassium salicylate.

Use of a ten-fold molar excess of potassium salicylate relative to oxalic acid produces an emission which approximates more to that of the curve with catalyst only (Fig. 7). In the hope of shortening the induction time while retaining a buffered solution, which is desirable for long term stability, a five fold molar excess of catalyst over inhibitor was examined and the maximum intensity was adjusted by varying the concentration of the oxalate in the range $1.5 \times 10^{-2}M$ to $2.5 \times 10^{-2}M$. The results are depicted in Fig. 8. Of these systems, the one with the highest concentration of oxalic acid ($5 \times 10^{-4}M$) had an unacceptable induction time of 50 minutes.

All other cases used the buffered additive of $5 \times 10^{-4}\text{M}$ potassium salicylate and 10^{-4}M oxalic acid. The most suitable system is considered to be that which uses $2 \times 10^{-2}\text{M}$ oxalate which has a maximum intensity of 30 units; with $2.5 \times 10^{-2}\text{M}$ oxalate this maximum reaches 35.5 units which is nearer the arbitrary upper limit necessary for concealment.

The stability of a stock solution without additives was examined over 12 months. A slight decline in maximum intensity occurred after six months storage (Fig. 9). This was a particularly promising result since buffered additives and radical scavengers would markedly improve long term storage life. In comparison to the TCPO systems, therefore, the oxalates (4) have the advantages of better solubility and storage. While the induction time of 5 minutes is not as short as desired it is still no worse than for TCPO.

The bis(trichlorocarboalkoxyphenyl)oxalates (2a-2d) were prepared by standard procedures. As with its counterpart (4d) the n-octyl derivative (2d) was a liquid which could not be purified without loss of CL performance. The isoamyl derivative (TCCPO; 2c) was considerably easier to handle during synthesis and purification than either (2a) and (2b) which have been used in commercial products. Again, little difference in light output was observed between the three oxalates (2a-2c). Preliminary attempts to modify the light emission were made using 10^{-1}M TCCAPO and hydrogen peroxide and concentrations of oxalic acid in the range $5 \times 10^{-2}\text{M}$ to 10^{-3}M (Fig. 10). Although this system held promise of reducing the induction time it was clear that at the concentration of oxalate used substantial quantities of additives would be required to modify the emission suitably. Under these circumstances small variations in concentration of components can change the light intensity sufficiently to render it difficult to remain consistently within the stipulated limits.

3. CONCLUSIONS

3.1 The susceptibility of bis(2-carboalkoxy-4,6-dinitrophenyl)oxalates to hydrolysis during storage makes these materials impractical for use in chemiluminescent lighting systems.

3.2 The intrinsically high intensity emissions from TCCPO and CPPO could not be satisfactorily modified to meet the requirements of a low intensity, long duration light source.

3.3 Members of the bis(2,4-dichloro-6-carboalkoxyphenyl)oxalate series exhibited suitable emission characteristics under the following conditions: oxalate ester $2 \times 10^{-2}\text{M}$; H_2O_2 , $2 \times 10^{-2}\text{M}$; potassium salicylate, $5 \times 10^{-4}\text{M}$; oxalic acid, 10^{-4}M . Although this system requires a 5 minute induction period before useful light outputs are achieved, it possesses superior storage stabilities and solubilities than does 2,4,6-TCPO.

4. EXPERIMENTAL

Proton magnetic resonance spectra were recorded at 60 MHz on a Varian HA 60 IL spectrometer with tetramethylsilane as internal reference, infrared spectra obtained with a Unicam SP200G instrument and mass spectra recorded using a Varian Associates MAT 111 system. The molecular weight determination was obtained using a modified Hewlett-Packard 302B Vapour Pressure Osmometer. All melting points are uncorrected. The microanalyses were performed by the Australian Microanalytical Service, CSIRO, Melbourne.

3,5-Dichlorosalicylic acid

Salicylic acid (500 g) was suspended in glacial acetic acid (2.5 L) and chlorine was passed through the stirred solution at a steady rate. The solids soon passed into solution but with further chlorination the mixture became cloudy. If water was added to the mixture at this stage a precipitate of 5-chlorosalicylic acid was obtained which could be recrystallised from ethanol as needles, m.p. 166-7° (lit. [19] m.p. 167.5°), ν max (Nujol) : 1660 cm^{-1} . Continued treatment with chlorine again clarified the solution and subsequently a crystalline precipitate formed. After a further 5 minutes the gas flow was ceased and the solution cooled in ice. The 3,5-dichlorosalicylic acid was collected by filtration, washed with water and then recrystallised from water to give white, granular crystals (603 g, 80.4%), m.p. 219.5° (lit. [17,20] m.p. 215, 219.5°), ν max (Nujol) : 1668 cm^{-1} .

Excessive chlorination eventually produced a yellow-orange colour in the solution. Addition of water to the filtrate obtained after collection of the dichloro acid gave a flocculent precipitate which on crystallisation from hexane afforded 2,4,6,6-tetrachloro-1,4-cyclohexadien-3-one as colourless plates, m.p. 123° (lit. [20,21] m.p. 122°) which was undepressed by admixture with an authentic sample [21]. ν max (Nujol) : 1700 cm^{-1} , δ (CCl_4): 3.65 Hz, *m/e* 230 (4-chlorine pattern). Found : C, 30.8; H, 0.9; O, 6.1; Cl, 61.6%. $\text{C}_6\text{H}_2\text{Cl}_4\text{O}$ requires C, 31.0; H, 0.9; O, 6.9; Cl, 61.2%.

Attempted synthesis of 3,5-dichlorosalicylic acid anhydride

3,5-Dichlorosalicylic acid (1 g) was heated under reflux with acetic anhydride (10 g) for 1 h and the mixture was allowed to stand overnight. The acetic anhydride was removed under reduced pressure to give an oil which did not solidify when cooled. The oil was repeatedly extracted with hot hexane and the cooled, bulked extracts deposited *acetyl 3,5-dichlorosalicylic acid* (0.73 g) which recrystallised from hexane as colourless crystals, m.p. 150-2°. ν max (KBr) : 1668, 1760 and 2500-3500 (broad) cm^{-1} ; δ (CDCl_3) : doublets centred at 7.98 and 7.68 ($J = 2.5$ Hz), 9.70 and 2.27; *m/e* : 248.

3,5,6-Trichlorosalicylic acid

(a) This compound was obtained essentially by Hanna's procedure [15] which involves chlorinating 3,5-dichlorosalicylic acid in 65% oleum at 70° with 0.0125 weight per cent of iodine as catalyst. The method was modified in that chlorination was carried out for 2 h at 70° followed by 4 h at 40°. The trichloro acid (81%) was recrystallised from methanol as colourless crystals, m.p. 208° (lit. [13] m.p. 207°), ν max (Nujol) : 1665 cm^{-1} .

(b) When 65% oleum was not available the synthesis proceeded satisfactorily if 3 to 4 times the quantity of 15% oleum was used.

(c) The method of Farinholt, Stuart and Twiss [13] recommends chlorinating the dichloro acid in 60% oleum at 80-90° for 15 h. In our hands this procedure afforded a mixture of products which were separated as follows. The cooled oleum solution was poured on to ice and the insoluble material was filtered to give a tan solid which was oven dried. The powdered solid was first extracted with hexane and the combined, dried (MgSO₄) extracts were taken to dryness to give 2,3,5,6-tetrachlorohydroquinol (3.5%), m.p. 234-6° (lit. [22] m.p. 236°), ν max (KBr) : 3400 (s) cm⁻¹, δ (CD₃COCD₃):8.80; m/e : 246 (4-Cl pattern). Acetylation with acetic anhydride gave the diacetate, m.p. 243-5° (lit. [23] m.p. 245°), ν max (KBr) : 1770 cm⁻¹; δ (CDCl₃) : 2.40; m/e : 330 (4-Cl pattern). The hexane-insoluble residue was repeatedly extracted with ether and the bulked, dried (MgSO₄) extracts were taken to dryness to afford 3,5,6-trichlorosalicylic acid (44%). Further extraction of the remaining solid with benzene led to the isolation of chloranil (10.8%), m.p. and mixed m.p. 290°d, from the benzene extracts. The insoluble residue of tri(3,5,6-trichlorosalicylide)(19%), was recrystallised from *o*-dichlorobenzene to m.p. 318-319°. ν max (KBr) : 1765 sh, 1780 cm⁻¹, Found: C, 37.9; H, 0.5%, (C₇H_{0.5}Cl₃)_x requires C, 37.6; H, 0.5%. The salicylide (2 g) was refluxed with potassium hydroxide (10 g) in a 4:1 ethanol-water mixture (50 ml) for 7 h and the solvent was then removed under reduced pressure. The residue was taken up in water and then acidified to give a precipitate of 3,5,6-trichlorosalicylic acid (1.9 g), m.p. 205-7°. Hydrolysis to the trichloro acid can be also achieved by heating the salicylide with sodium hydroxide for 24 h. A MW of 630 ± 60 was obtained by vapour pressure osmometry using *o*-dichlorobenzene as solvent, cholesterol as the calibration standard and an operating temperature of 70°.

(d) Attempts were made to avoid the formation of byproducts obtained in (c) by using reactions times of 3 to 8 h. In one case a mixture of 5-chloro- and 3,5-dichlorosalicylic acid was chlorinated in oleum and the cooled mixture was poured on to ice to give a precipitate of 5-chloro-3-sulfosalicylic acid hydrate, m.p. 172-173°. This compound was soluble in water and ethanol and had ν max (KBr) : 2850 (broad), 1670, 1190 (broad) and 1040 cm⁻¹; δ (CD₃COCD₃) : 7.97; m/e : 252. Found : C, 31.4; H, 2.8; Cl, 13.5%. C₇H₇O₇SCl requires : C, 31.1; H, 2.6; Cl, 13.1%.

Attempted synthesis of 3,5,6-Trichlorosalicylic acid anhydride

3,5,6-Trichlorosalicylic acid (1.3 g) was heated under reflux with acetic anhydride (15 ml) for 30 minutes. The mixture was cooled and excess acetic anhydride was distilled off under reduced pressure. The residual oil solidified on cooling and was recrystallised from hexane to give acetyl acetic 3,5,6-trichlorosalicylic anhydride (1.2 g) as colourless needles, m.p. 79-80°. ν max (KBr) : 1745, 1775 and 1815 cm⁻¹; δ (CDCl₃) : 7.65, 2.32 and 2.30 integrating for 1:3:3. The same product was also obtained when the trichloro acid was warmed at 60° for 5 minutes with acetic anhydride containing a few drops of conc. sulphuric acid.

3,5-Dinitrosalicylic Acid

The method of Meldola, Foster and Brightman [24] afforded this compound as a pale yellow solid (75%), m.p. 173-4° (lit. [25] m.p. 173°). The reaction proceeds satisfactorily below 25° but at temperatures in excess of 40° the product is picric acid.

Salicylate Esters

(a) Attempted esterification of 3,5,6-trichlorosalicylic acid with *n*-butanol by heating under reflux in the presence of conc. H₂SO₄ was unsuccessful.

(b) Esterification proceeded smoothly with the following general method.

The salicylic acid (0.2 mole), alcohol (2.5 mole) and conc. H₂SO₄ (10 g) were heated under reflux for 24 h and the generated water removed with a Dean-Stark apparatus. The cooled mixture was filtered to remove unreacted acid and then worked up by the modifications described below. Physical constants of the products are listed in Table 1.

- (1) The filtrate was poured into water and extracted with petroleum ether (b.p. 60-80°). The dried (MgSO₄) extracts were concentrated under reduced pressure and then fractionally distilled. The ester was obtained after a forerun of dialkyl ether. Some decomposition may occur at high distillation temperatures and in the cases of the pentyl and 3'-methylbutyl 3,5,6-trichlorosalicylates significant quantities of 2,4,5-trichlorophenol were collected prior to the ester distillate. In some cases the residue after removal of the ether was passed through an alumina column but this procedure was time-consuming and the purity of the ester was no better than from distillation. Column chromatography was used for the following liquid esters: octyl 3,5-dichlorosalicylate, and pentyl, 3'-methylbutyl and octyl 3,5,6-trichlorosalicylate.
- (2) The reaction mixtures containing the butyl and 3'-methylbutyl 3,5-dinitrosalicylates were poured into hexane or water and the collected precipitates were recrystallised from small volumes of ether to give almost colourless solids. The pentyl ester separated as an oil when the reaction mixture was poured into water. The oil solidified on cooling and was filtered off and dissolved in chloroform. The dried (MgSO₄) solution was concentrated under reduced pressure and the resulting oil was recrystallised from petroleum ether (b.p. 40-60°). The esters of 3,5-dinitrosalicylic acid decompose vigorously on heating and attempts to distil these compounds were abandoned.
- (3) The butyl, pentyl and 3'-methylbutyl 3,5-dichlorosalicylates were obtained by pouring the reaction mixture into chilled A.R. methanol (600 ml). The products either precipitated immediately or after further cooling in an ice-bath. Butyl 3,5,6-trichlorosalicylate was best obtained by pouring the reaction mixture on to ice. The separated organic layer was dissolved in petroleum ether (b.p. 60-80°), dried (MgSO₄), the solvent was removed and the ester was then recrystallised from petroleum ether (b.p. 40-60°).

(c) The alternative synthetic approach described below was also briefly examined.

Dimethylformamide (DMF; 4 g, 0.05 mole) was added dropwise to a stirred suspension of 3,5,6-trichlorosalicylic acid (48 g, 0.2 mole) in thionyl chloride (36 g, 0.3 mole) over a period of 10 minutes. The mixture was refluxed for a further 3 h and then allowed to stand overnight. Excess thionyl chloride and DMF were removed under reduced pressure and the residue was then heated under reflux with n-butanol (0.5 mole) for 24 h. The cooled mixture was poured into water and the organic layer was taken up in hexane. Water insoluble tri(3,5,6-trichlorosalicylide) (3.5 g) was filtered off and the hexane layer was then treated as in (b (3)) above to afford the butyl ester (30.4 g, 51%).

Oxalyl Chloride

Oxalyl chloride was obtained by the method of Staudinger [26]. Commercial oxalyl chloride (Aldrich) was used without further purification.

Oxalate Esters

Before use the salicylate esters were rigorously dried under vacuum in the presence of a drying agent such as "Sicapent" (Schuchardt). The following general procedure was then used in all cases. Solutions of the salicylate ester (0.1 mole) in sodium dried, redistilled benzene (100 ml) and freshly distilled triethylamine (0.1 mole) were introduced into a vacuum dried flask under nitrogen. Oxalyl chloride (0.06 mole) in dry benzene (20 ml) was added dropwise over 30 minutes using a pressure equalizing funnel and the mixture was then stirred a further 3 to 6 h at room temperature. The precipitate of triethylamine hydrochloride was collected by filtration and the filtrate was either concentrated and treated with dry hexane (as in the dinitro series) or taken to dryness and the residue recrystallized repeatedly from dry hexane. All work-up operations were carried out under anhydrous conditions. The products are listed in Table 2.

Oxalate esters of this type are prone to hydrolysis and even slight traces of hydrolysis products adversely affect the CL emission of the materials. It is therefore essential to store the oxalates under scrupulously anhydrous conditions. The method used in this study was to place the oxalate ester in a dried container sealed with a bakelite screw top lid. This container was then stored over "Sicapent" in an evacuated desiccator.

Chemiluminescence Measurements

Dimethyl phthalate was fractionally distilled before use. A stock solution of 0.66M hydrogen peroxide in dimethyl phthalate was prepared and assayed as described previously [18].

Before intensity measurements were carried out the appropriate weight of oxalate ester in dimethyl phthalate containing $1 \times 10^{-3}M$ 9,10-bis(phenylethynyl) anthracene [18] was heated at 150° for 1 h to decarboxylate any hydrolysis products of the oxalate ester [4]. Test solutions were prepared by introducing the required quantity of additive in dimethyl phthalate into the solution of the oxalate. The total volume was made up to 10 ml with dimethyl phthalate containing $1 \times 10^{-3}M$ 9,10-bis(phenylethynyl) anthracene.

Light intensity decay curves were obtained by introducing the requisite quantity of 0.66M hydrogen peroxide in dimethyl phthalate from a calibrated syringe into the calculated volume of oxalate solution and transferring an aliquot to a 10 mm quartz cell. Measurements were performed on an Aminco-Bowman spectrophotofluorometer without external excitation and operated at an emission wavelength of 513 nm. Relative intensity readings were obtained in arbitrary units with the following fixed settings: photo-multiplier 0.5; meter multiplier 0.03; cell shutters 0.5 mm; sensitivity 0. Measurements were taken at $20 \pm 1^\circ\text{C}$.

The intensity limits for the low intensity system were ascertained following subjective tests under dark-room conditions using a 1 x 10 cm fluorescence cell containing the chemiluminescing solution. It was found that a light output of less than 8 units in intensity was not sufficient to decipher instrument scales or read a printed page. Above the upper limit of 40 units the emission is visible from 50 metres.

5. ACKNOWLEDGEMENTS

We gratefully acknowledge the technical assistance of Mr. P.J. Hanhela and Mrs. R.M. Holdsworth. Proton magnetic resonance spectra were recorded by Dr. A.G. Moritz, mass spectra by Dr. A.J. Power, and the molecular weight determination was obtained by Dr. C.E.M. Morris.

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T A B L E 1

SALICYLATE ESTERS

Salicylate Ester	Yield (%)	m.p. (°C)	ν max (cm ⁻¹)	δ (CDCl ₃)
Butyl 3,5-dinitrosalicylate	62	59 ^a	1685	8.93(s), 4.52(t), 1.25-2.08(m), 1.07(d) ^e
Pentyl 3,5-dinitrosalicylate	55	33-33.5	1680	8.92(s), 4.48(t), 1.20-2.1(m), 1.10
3'-Methylbutyl 3,5-dinitrosalicylate	65	60-61.5	1680	8.7(s), 4.48(m), 1.60-2.0(m), 1.02(d) ^e
Butyl 3,5-dichlorosalicylate	65	49-52	1675	
Pentyl 3,5-dichlorosalicylate	50	35-38	1670 ^c	7.61(d) ^d , 7.39(d) ^d , 4.32(t), 3.33(t), 0.83-2.0(m)
3'-Methylbutyl 3,5-dichlorosalicylate	50	52-53	1680	7.66(d) ^d , 7.47(d) ^d , 4.38(t), 1.70(m), 0.97(d) ^e
Octyl 3,5-dichlorosalicylate	46	-	1675 ^c	7.70(d) ^d , 7.48(d) ^d , 4.34(t), 3.37(t), 1.30(m), 0.92(d) ^e
Butyl 3,5,6-trichlorosalicylate	67	39-41 ^b	1745,1655	7.57(s), 4.43(t), 1.3-1.9(m), 1.04(d) ^e
Pentyl 3,5,6-trichlorosalicylate	43	b ₁ 185-190	1735,1660 ^c	
3'-Methylbutyl 3,5,6-trichlorosalicylate	48	b ₂ 171-177	1735,1655 ^c	7.43(s), 4.33(q), 1.70(m), 0.95(d) ^e
Octyl 3,5,6-trichlorosalicylate	52	-	1740,1665 ^c	7.58(s), 4.42(t), 3.37(t), 1.29(m), 0.97(d) ^e

^alit [4] m.p.59-60°; ^blit [4] m.p.38-41°; ^cliquid film, all other spectra taken in nujol; ^d_J = 2.8 Hz; ^e_J = 6 Hz.

TABLE 2

OXALATE ESTERS

Oxalate	m.p. (°C)	Yield (%)	ν_{\max} (cm ⁻¹)
Bis(2,4-dinitro-6-carbobutoxyphenyl)	140 ^a	33	1795,1725
Bis(2,4-dinitro-6-carbo[3'-methylbutoxyl]phenyl)	153-4	38	
Bis(2,4-dinitro-6-carbopentoxyphenyl)	141.5-142	30	
Bis(2,4-dichloro-6-carbobutoxyphenyl)	60-61	72	1780,1770,1715,1705
Bis(2,4-dichloro-6-carbo[3'-methylbutoxy]phenyl)	80-80.5	78	1775,1710
Bis(2,4-dichloro-6-carbopentoxyphenyl)	liquid	56	1790,1770,1665 ^d
Bis(2,4-dichloro-6-carbooctyloxyphenyl)	liquid	60	1800,1780,1720,1675 ^d
Bis(2,4,5-trichloro-6-carbobutoxyphenyl)	121-123 ^b	53	1780,1735
Bis(2,4,5-trichloro-6-carbo[3'-methylbutoxy]phenyl)	101-103	70	1780,1735
Bis(2,4,5-trichloro-6-carbopentoxyphenyl)	85 ^c	65	1790,1735
Bis(2,4,5-trichloro-6-carbooctyloxyphenyl)	liquid	65	1810,1780,1740

^a lit.⁴ m.p. 139-141°; ^b lit.⁴ m.p. 120-123°; ^c lit.⁴ m.p. 84-86°;

^d liquid film; all other measurements taken from nujol mull.

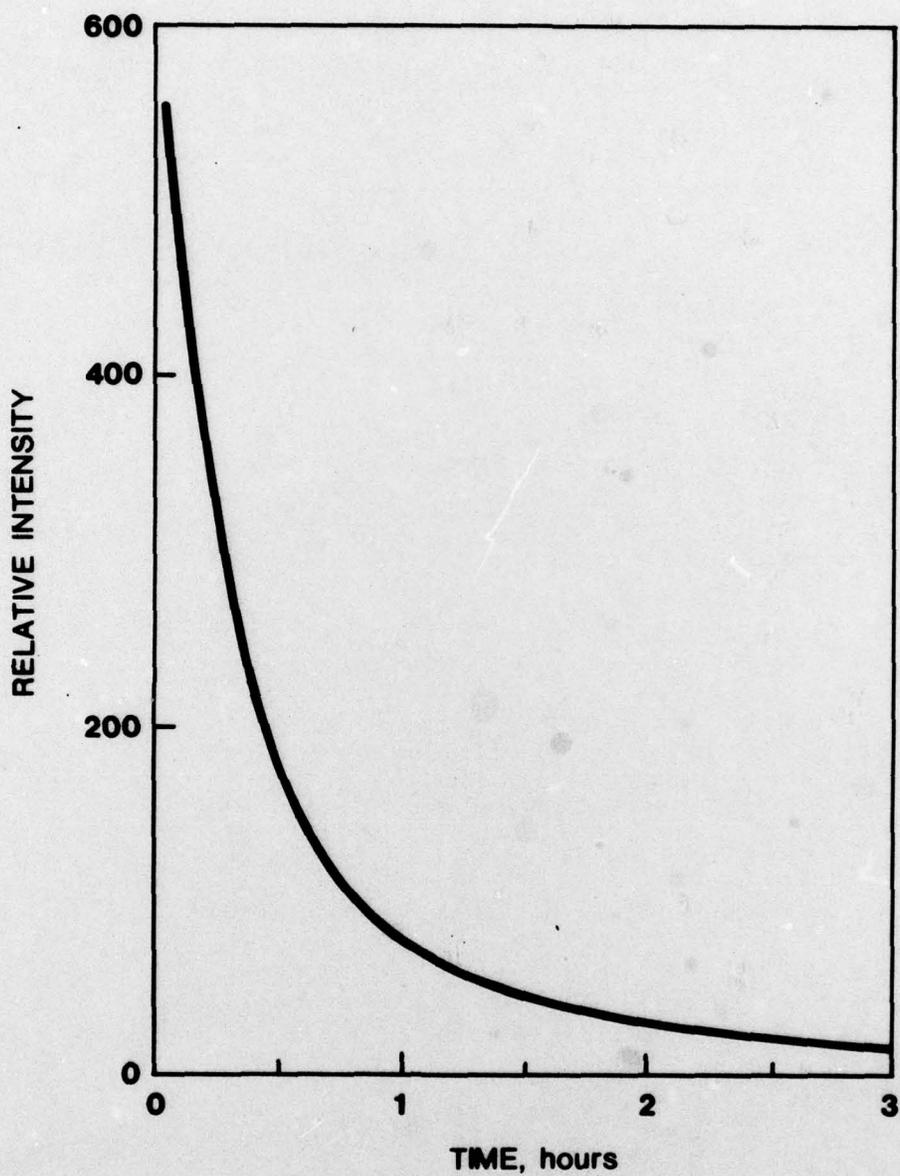


FIG. 1 - CL emission intensity decay curve from bis(2,4-dinitro-6-carbobuoxyphenyl)oxalate ($10^{-2}M$) and H_2O_2 ($10^{-2}M$) in DMP containing BPA ($10^{-3}M$).

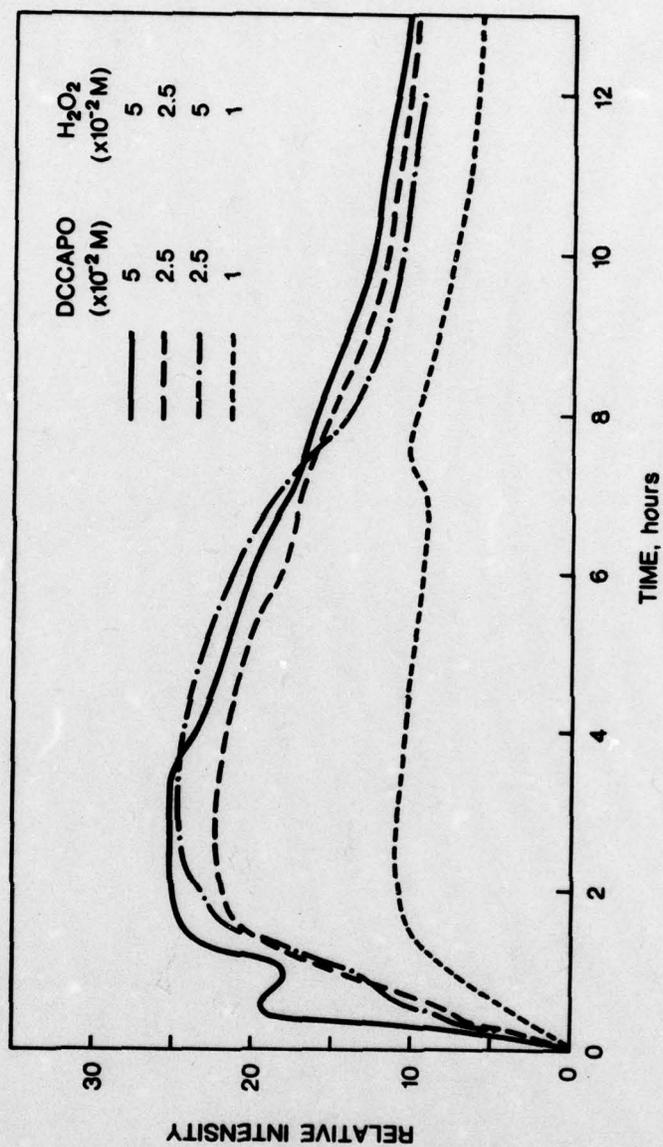


FIG. 2 - CL emission decay curves from DCCAPO and H₂O₂ in DMP containing BPA (10⁻³M).

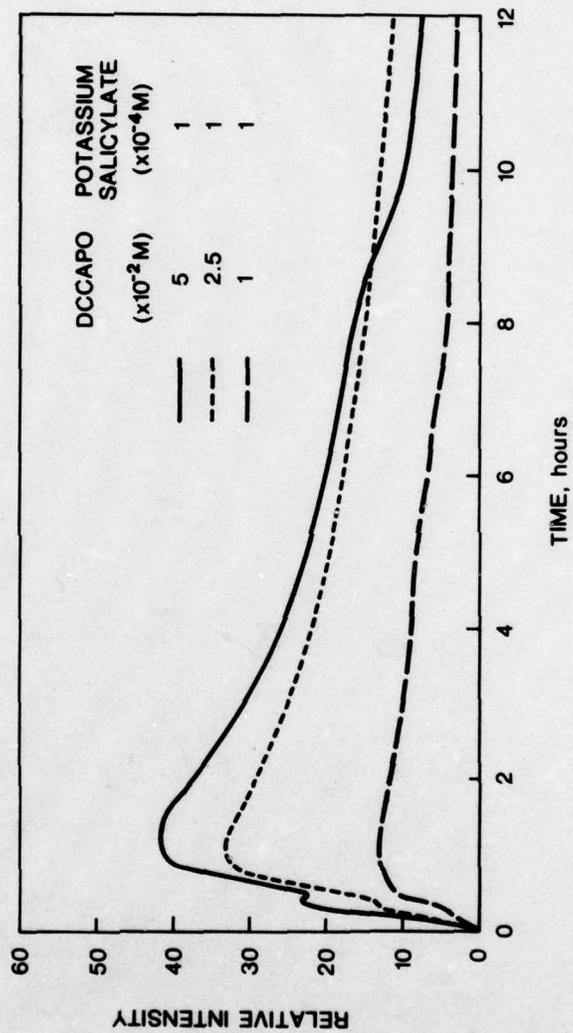


FIG. 3 - CL emission decay curves from DCCAPO, H₂O₂ and potassium salicylate (10⁻⁴M) in DMP containing BPA (10⁻³M).

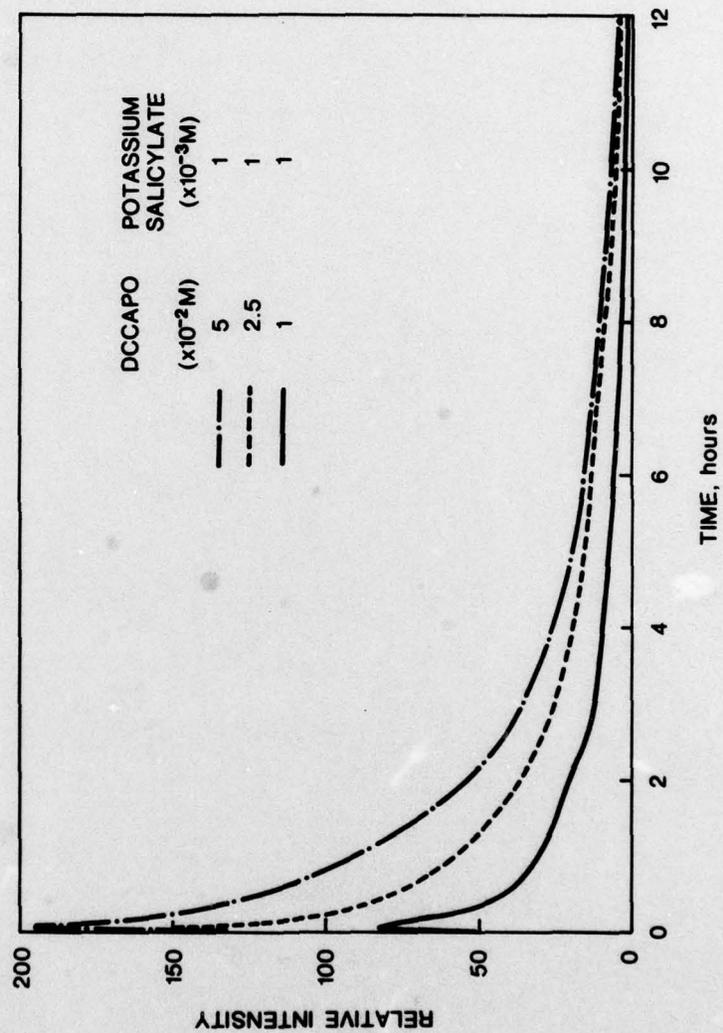


FIG. 4 - CL emission decay curves from DCCAPO, H₂O₂ and potassium salicylate (10⁻³M) in DMP containing BPA (10⁻³M).

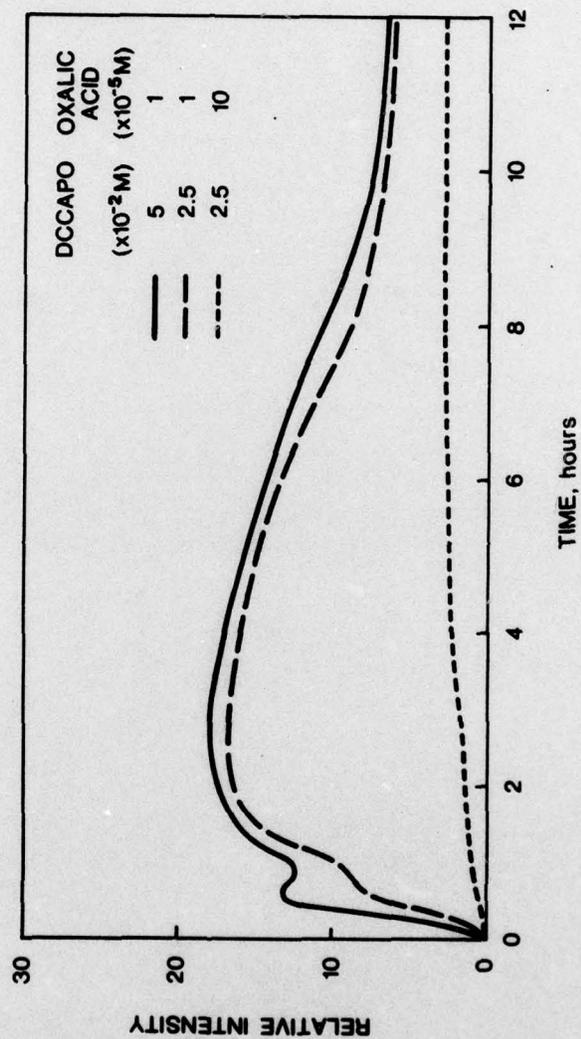


FIG. 5 - CL emission decay curves from DCCAPO, H₂O₂ and oxalic acid in DMP containing BPA (10⁻³M).

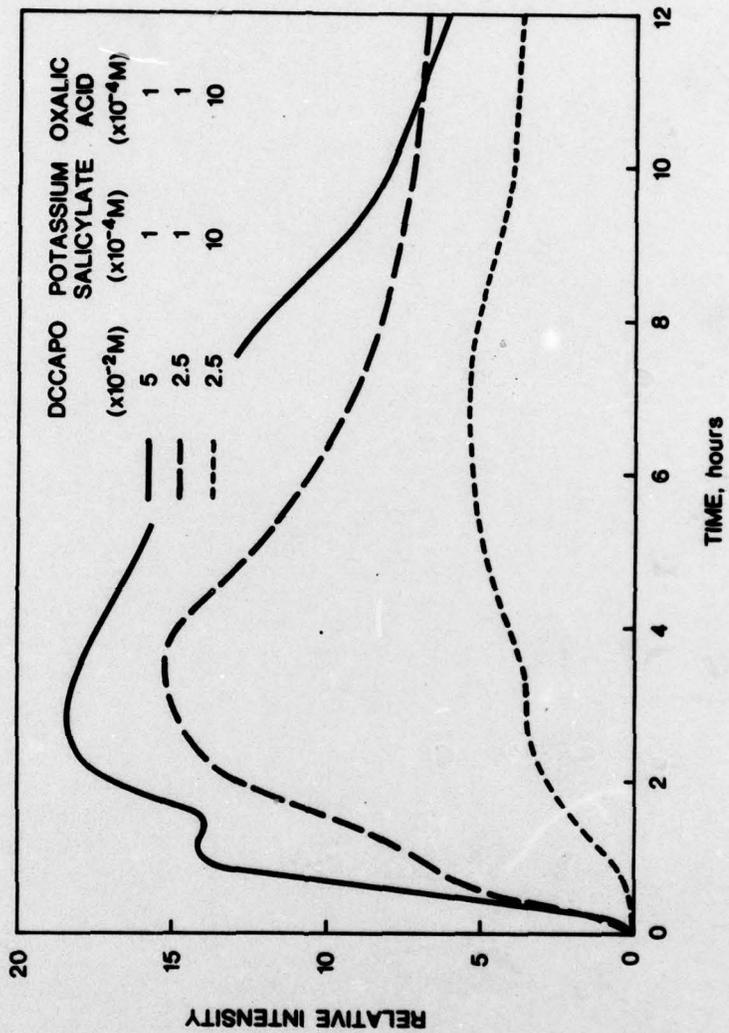


FIG. 6 - CL emission decay curves from DCCAPO and H_2O_2 in DMP containing BPA ($10^{-3}M$) together with equimolar concentrations of potassium salicylate and oxalic acid.

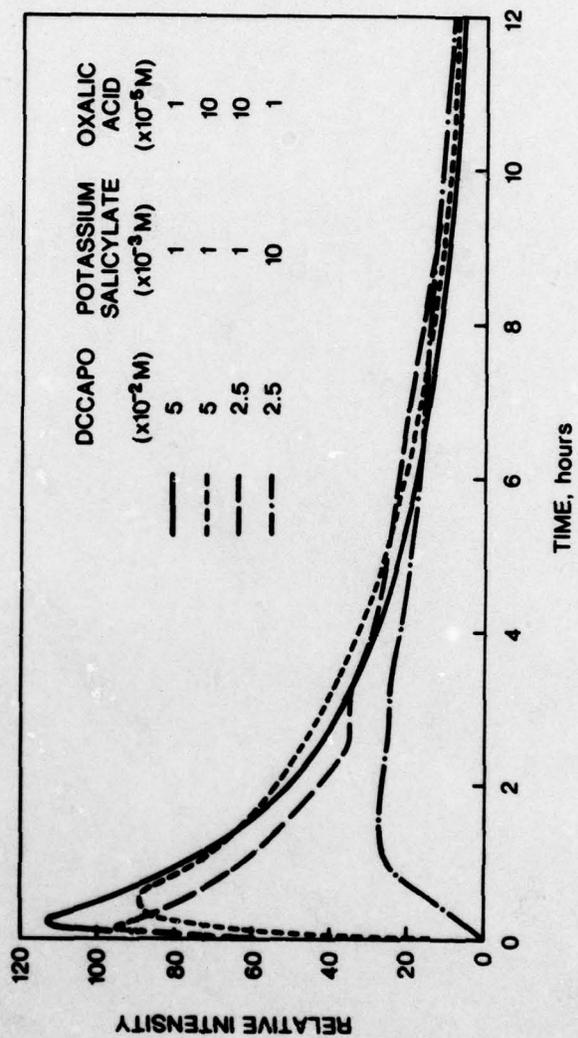


FIG. 7 - CL emission decay curves from DCCAPO and H_2O_2 in DMP containing BPA ($10^{-3}M$), potassium salicylate and oxalic acid - oxalic acid in excess.

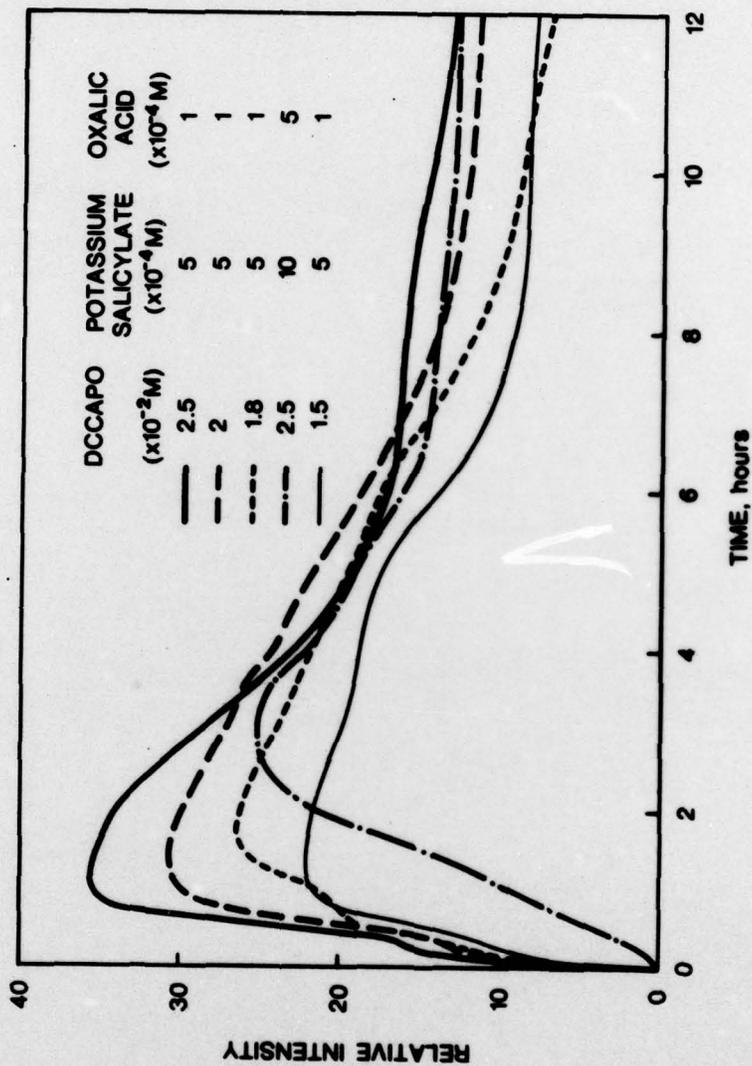


FIG. 8 - CL emission decay curves from DCCAPO and H₂O₂ in DMP containing BPA (10⁻³M) with optimised concentrations of potassium salicylate and oxalic acid.

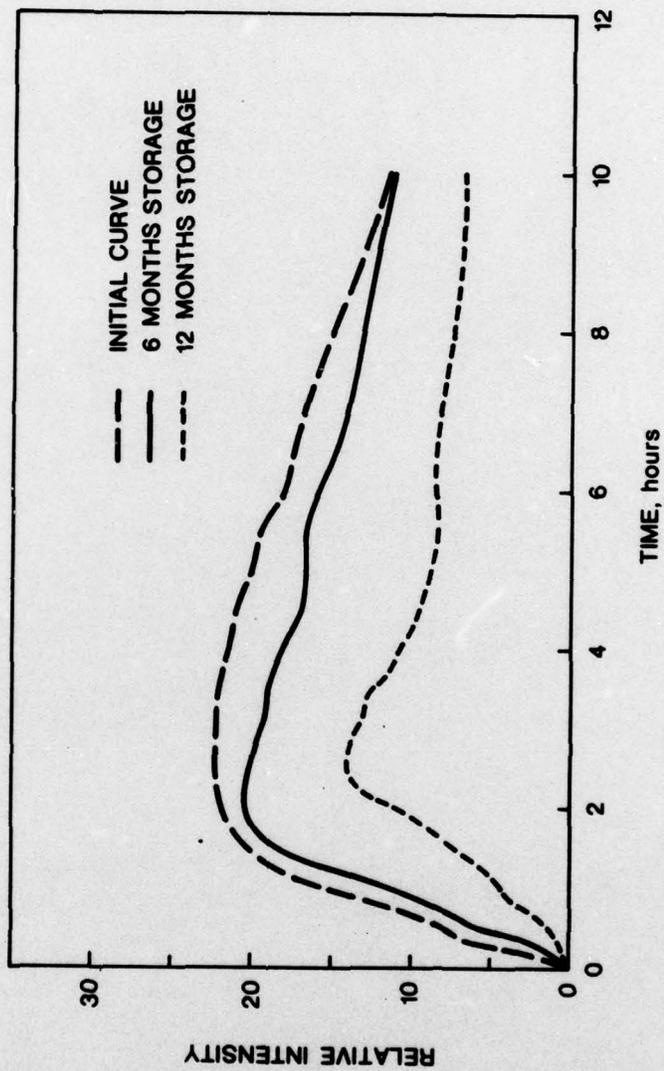


FIG. 9 - Change in CL emission decay curve from DCCAPO ($2.5 \times 10^{-2}M$) and H_2O_2 ($2.5 \times 10^{-2}M$) in DMP containing BPA ($10^{-3}M$) after storage for 12 months.

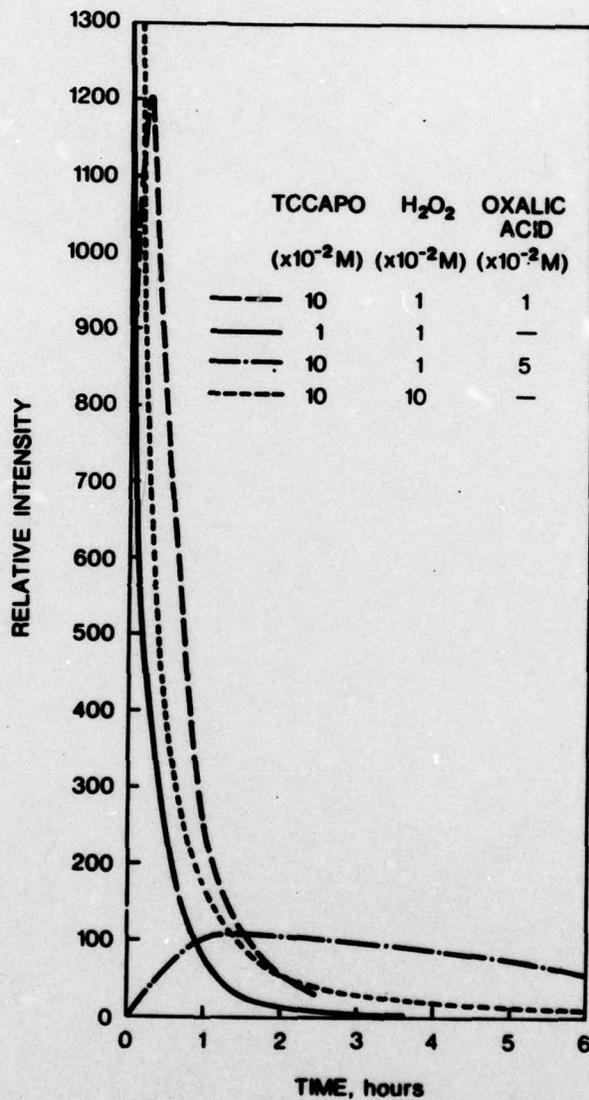


FIG. 10 - CL emission decay curves from TCCAPO and H₂O₂ in DMP containing BPA (10⁻³M) both with and without oxalic acid.

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